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PRODUCTION OF JET FUELS FROM COAL DERIVED LIQUIDS

VOL V - Recovery of Benzene/Benzene Plus Phenol From The Great Plains Gasification Plant Crude Phenol Stream

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In September 1986, the Fuels Branch of the Aero Propulsion Laboratory at Wright-Patterson Air Force Base, Ohio, commenced an investigation of the potential for production of jet fuels from the liquid by-product streams produced by the gasification of lignite at the Great Plains Gasification Plant located in Buelah, North Dakota. Funding was provided to the U. S. Department of Energy (DOE) Pittsburgh Energy Technology Center (PETC) to administer the experimental portion of this effort. This report details the program with Hydrocarbon Research, Inc. (HRI), a subcontractor to Burns and Roe Services Corporation, who, as a subcontractor to DOE, investigated the potential of producing benzene or benzene plus phenol from the crude phenol stream. The production of chemicals from the crude phenol stream can be used in a scenario where chemical production subsidizes the production costs associated with producing jet fuels and the fuels can be marketed at prevailing price.

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FOREWORD

In September 1986, the Fuels Branch of the Aero Propulsion Laboratory at Wright-Patterson Air Force Base, Ohio, commenced an investigation of the potential for production of jet fuel from the liquid by-product streams produced by the gasification of lignite at the Great Plains Gasification Plant located in Buelah, North Dakota. Funding was provided to the U. S. Department of Energy (DOE) Pittsburgh Energy Technology Center (PETC) to administer the experimental portion of this effort. This report details the efforts of Hydrocarbon Research, Inc. (HRI), as a subcontractor to Burns and Roe Services Corporation, who, as a subcontractor to DOE (DOE Contract Number DE-AC22-84PC-72571), studied the potential of the crude phenol stream for the production of benzene or benzene plus phenol which could subsidize the production costs associated with the production of jet fuels. DOE/PETC was funded through Military Interdepartmental Purchase Request (MIPR) FY1455-86-N0657. Mr. William E. Harrison III was the Air Force Program Manager, Mr. Gary Stiegel was the DOE/PETC Program Manager and Mr. Everette C. Harris was the HRI Program Manager.

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EXECUTIVE SUMMARY

Hydrocarbon Research, Inc. (HRI) successfully completed a Dynaphen process feasibility study for Burns and Roe Services Corporation. The program utilized HRI's Dynaphen^{sm} Technology for processing Great Plains Coal Gasification Plant (GPGP) crude phenol. This investigation was part of the United States Department of Defense's (DOD) overall program to evaluate the potential production of military jet fuel from GPGP liquid by-products.

As of January 1988, GPGP was producing approximately 900 barrels per day of crude phenols. Untreated, this stream has very little commercial value. Preliminary technical and economic evaluations performed by J. E. Sinor Consultants Inc.[1] indicated the Dynaphen^{sm} Process had a potential for nearly a 30% discounted cash flow rate of return, a higher return than any of the other crude phenol processes evaluated.

The program was divided into four operational tasks; feedstock analysis, a process variable study, a continuous once-through test and a demonstration recycle test. Results from each of these tasks are discussed in detail later.

The feasibility of Dynaphen^{sm} processing of GPGP crude phenol was demonstrated in this program. Major accomplishments include a successful demonstration recycle run with near-extinction-recycle that produced a liquid product stream that was more than 95 W % benzene, phenol and water. Total benzene and phenol yields in excess of 73 V % were achieved by first distilling the as-received crude phenol and then Dynaphen processing the distillation bottoms. Single-pass cut phenol operating conditions were found which increased the amount of phenol in the feed stream by more than 50%.

A total of 13 process conditions were evaluated in the process variable study, examining temperature, feed phenolic and water content, pressure and residence time effects. The phenol concentration in the as-received feedstock was too high to produce additional phenol at the process conditions studied. A distillation, which removed about two-thirds of phenol produced a bottoms stream with less than 20 W % phenol. In the process variable study 6 operating conditions with this cut phenol feed demonstrated net phenol production.

PROGRAM DESCRIPTION AND BACKGROUND

INTRODUCTION

Hydrocarbon Research, Inc. (HRI) was contracted by Burns and Roe Services Corporation in September 1987 to perform experimental work utilizing Dynaphen[sm] Technology for processing Great Plains Coal Gasification Plant (GPGP) crude phenol stream. This investigation was part of the United States Department of Defense's (DOD) overall program to evaluate the potential production of military jet fuel from GPGP liquid by-products.

As of January 1988, GPGP was producing approximately 900 barrels per day of crude phenols. This phenol stream contains non-phenolic components, such as aromatic hydrocarbons and nitrogen-containing hydrocarbons. Untreated, this stream has very little commercial value. Technical and economic evaluations performed by J. E. Sinor Consultants Inc.[1] indicated the Dynaphen Process had a potential for nearly a 30% discounted cash flow rate of return, a higher return than any of the other crude phenol processes evaluated.

HRI has been a pioneer in the development of aromatics hydrodealkylation technology for almost thirty years, beginning with the fundamental research and development of HRI/ARCO Technology's patented "HDA" Process in the 1950's, which has now been licensed and successfully operated in twenty-six plants around the world.

HRI began development and subsequent patenting of the Dynaphen[sm] Process in the 1970's. Previous experimental studies have investigated model compounds and Sasol I crude phenol.

Benzene and phenol yields can be increased by recycling of the unconverted cresylic acids, toluene, xylene and ethylbenzene. The intent of the current program was to establish a process variable data base with GPGP crude phenol, to demonstrate positive phenol make and to further the commercial readiness of the Dynaphen Process by demonstrating recycle operations at conditions which have commercial viability with this readily available feedstock.

OBJECTIVES

The objectives of this experimental program were:

1. Demonstrate Dynaphen^{sm} Process technology on GPGP crude phenol.
2. Acquire benzene and phenol yields while conducting a process variable study.
3. Conduct a single pass operation to generate recycle material for a demonstration test.
4. Demonstrate recycle Dynaphen^{sm} Process operation.
5. Acquire product quality data from selected liquid products.

SCOPE OF WORK

To achieve the program objectives, the scope of work was divided into 5 tasks. These were:

Task 1 - Feedstock Analysis and Preparation

Laboratory analyses characterized the three different phenolic streams examined in this program.

- As-Received Crude Phenol
- A Nominal 365°F$^+$ Cut Of The As-Received Crude Phenol
- A Phenolic Recycle Stream

Five different combinations of these phenolic streams were then prepared and processed.

Task 2 - Process Variable Study

A 13-point test matrix examined the effect of several process variables. Reactor temperature was studied with both the as-received crude phenol and the nominal 365°F$^+$ cut. Additional experiments were made to quantify the effects of pressure and residence time.

Task 3 - Continuous Once-Through Test

The goal of this task was to generate material for recycle in the demonstration test. Yield data from Process Variable Study were utilized in the selection of the operating conditions for this task.

Task 4 - Demonstration Recycle Test

Task 4 consisted of a simulated demonstration of Dynaphen^{sm} Process recycle operations.

Task 5 - Final Report

This report was the last task in the scope of work.

PROCESS DESCRIPTION

HDA Process Experience

Atlantic Richfield Corporation (ARCO) and Hydrocarbon Research, Inc. (HRI) have been jointly engaged in the development, licensing and engineering of aromatics technologies for over 25 years. Their combined technology resources include the HDA Process (hydrodealkylation). HRI and ARCO have more than 20 licensed HDA units in at least 15 different countries with throughputs generally between 1,000 and 9,000 barrels per day. Typical feedstocks include toluene, pyrolysis gasolines and coke oven light oils.

Dynaphen^{sm} Process Description

Dynaphen^{sm} is the trade name given to a process developed by Hydrocarbon Research, Inc. (HRI®) for the thermal hydrodealkylation of cresylic acids (alkylphenols). The process is an extension of HRI's commercially proven HDA™ (HydroDeAlkylation) technology for

the conversion of alkylaromatics to benzene and fuel gas. The same basic reactor technology, utilizing a pressurized, high-temperature, non-catalytic hydrodealkylation reactor, is applied in the Dynaphen Process to the hydrodealkylation of alkylphenols derived from a variety of materials, notably coal liquids. The Dynaphen reactor primarily dealkylates the cresylic acid molecules, although some dehydroxylation occurs as well. Dehydroxylation products (i.e., toluene and xylene), plus the unconverted alkylphenols are recycled to the Dynaphen reactor so that the major reactor products are phenol and benzene.

In brief, the chemistry which occurs in Dynaphen and HDA reactor systems can be represented by the reactions below:

1. Toluene + Hydrogen --> benzene + methane
   (has a theoretical 84.8 W % benzene yield)

2. Cresol + Hydrogen --> phenol + methane
   (has a theoretical 87.0 W % phenol yield)

3. Cresol + Hydrogen --> benzene + methane + water
   (has a theoretical 72.2 W % benzene yield)

Reaction 1 is the typical HDA reaction while Reactions 2 and 3 both occur in the Dynaphen^{SM} Process. Theoretical yields become progressively lower as the degree of feedstock hydroxylation and alkylation increase. Since Dynaphen feedstocks tend to be more substituted than HDA feedstocks, theoretical Dynaphen yields tend to be lower than theoretical HDA yields. Further details are presented in Appendix A.

Figure 1 illustrates a basic flow scheme of the Dynaphen Process. The alkylphenolic feed to the process is mixed with hydrogen and sent to the Dynaphen preheater and reactor. The reactor effluent is cooled by exchange with reactor feed (and other process streams) for heat recovery, and is separated into vapor- and liquid-phase components. Some light gas is produced in this process, mostly methane and some carbon monoxide. A portion of this off-gas is fed to the hydrogen plant to produce hydrogen gas required by the process. The balance of this off-gas is used within the plant to supply part of the process fuel requirement.

The liquid reactor effluent may be sent through a stabilizer and a clay tower before distillation. Benzene and phenol are recovered in two series-connected distillation towers. Unconverted alkylphenols are recycled to the Dynaphen reactor. Dehydroxylation by-products, primarily toluene and xylene, are also recycled, eventually producing benzene. Thus, the net products of the Dynaphen system are benzene and phenol.

Experiments using real and simulated commercial feedstocks were run at the HRI Research and Development Center in 1979-81. Phenolsolvan extracts from the Lurgi gasifiers at SASOL in South Africa (similar in composition to the Great Plains crude phenols) were studied, as were H-Coal® liquefaction products and steam cracker tars from an oil refinery. In addition, mixtures of phenol, methylphenols and ethylphenols were blended to simulate the distribution of these materials in coal liquefaction by-products. Total projected liquid yield (phenol and benzene) from these early experiments was approximately 80% (by weight of feed). The weight ratio of phenol to benzene in the total liquid product was approximately 1.8 to 1.[2]

HRI's early development work[3-7] on the Dynaphen Process was carried out at the time when extensive R&D work was being done on coal liquefaction (e.g., H-Coal®, Exxon Donor Solvent, SRC-I, SRC-II), and funds were available to evaluate techniques for upgrading by-products such as phenols. With the decline of coal liquefaction work in recent years, interest in ancillary processes declined as well, and so no Dynaphen studies were carried out between 1982 and 1987 when the current program was initiated.

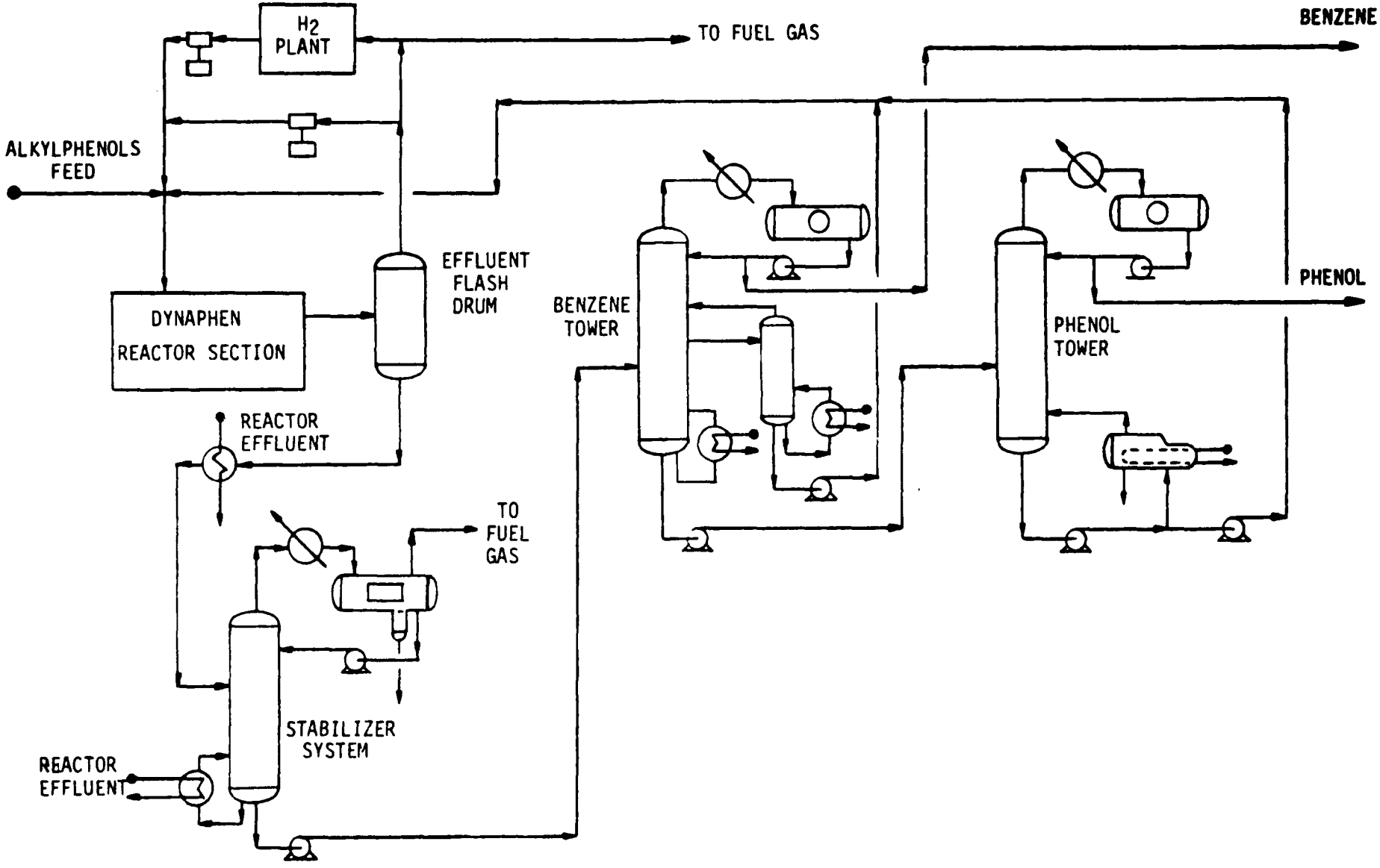


FIGURE 1. BASIC DYNAPHEN FLOW SCHEME

TECHNICAL PROGRAM

TECHNICAL SUMMARY

The data developed from this Dynaphen[sm] Process feasibility program contain consistent and key information which can be used to provide a sound basis for process optimization with respect to phenol, benzene, or phenol plus benzene yields.

In particular, high conversion data from the demonstration recycle operations indicate near-extinction-recycle operation is feasible. Data obtained from a process variable study show the effects of temperature, reactor feed phenolic and water content, pressure and residence time on the yield slate.

Additional work will be required before commercialization is accomplished. This to include optimization of reaction conditions and separation techniques, kinetic model development, engineering and economic evaluation.

TASK 1 - FEEDSTOCK ANALYSIS AND PREPARATION

HRI received one 55-gallon drum of crude phenol to use as feedstock for this experimental program in October 1987. The material was obtained from A.N.G. Coal Gasification Company of Bismarck, North Dakota.

Five different reactor feed combinations were tested during this experimental program. These were:

1. The as-received crude phenol, herein designated as HRI No. 5511 and as crude phenol. This feed was used in Runs 42-46.

2. A nominal 365°F$^+$ cut of HRI No. 5511, herein designated as L-731 and as cut phenol. This feed was used in Runs 47-49.

3. A solution of 92 W % L-731 and 8 W % de-ionized water. This feed was used in Runs 50-54.

4. A solution of 90 W % L-731 and 10 W % de-ionized water. This feed was used the continuous once through test, Run 60.

5. A solution of 74.9 W % L-731, 15.1 W % recycle material and 10 W % de-ionized water. This feed was used in the recycle test, Run 61.

The three different phenolic streams examined in this program were characterized by laboratory analyses. These inspections are presented in Table 1 and Figure 2.

Analysis of the two phenol feeds included API gravity, elemental analysis (C,H,N,S), Karl Fischer water, D-1160 vacuum distillation, TBP distillation, thermogravimetric analysis and liquid gas chromatograghy analysis.

The nominal 365°F$^+$ feed cut was produced using a TBP-type still. This cut corresponded to 66.54 W % of the as-recieved crude phenol.

The recycle stream was a combination of the 375°F$^+$ cut of the Run 60 liquid product and pure toluene, xylene and ethylbenzene. This is further discussed in Task 4 of the Technical Program.

TABLE 1. FEEDSTOCK ANALYSIS

MATERIAL	HRI No. 5511	L-731[1,2]
DESCRIPTION	GPGP CRUDE PHENOL	CUT FEED
API	1.2	-1.2
W % WATER	4.96	0.00
ELEMENTAL ANALYSIS, WET BASIS		
Carbon	72.5	72.3
Hydrogen	7.3	6.8
Nitrogen	0.5	0.5
Sulfur	0.07	0.07
Oxygen (By Difference)	19.63	20.33
D-1160 VACUUM DISTILLATION		
IBP, °F	154	381
IBP-355°F, W %	7.5	0.0
355-450°F, W %	63.1	61.3
450-600°F, W %	22.6	24.3
Residue at 600°F, W %	6.8	14.4
TBP DISTILLATION		
IBP, °F	144	187
IBP-355°F, W %	10.8	1.3
355-365°F, W %	38.0	10.0
365-400°F, W %	21.1	39.5
400-450°F, W %	6.2	13.5
Residue at 450°F, W %	23.9	35.7
TGA ANALYSIS		
IBP-212°F, W %	5.3	1.8
212-302°F, W %	20.2	12.1
302-392°F, W %	52.8	40.0
392-482°F, W %	16.0	30.4
482-662°F, W %	2.2	5.6
662-932°F, W %	0.7	2.3
Residue at 932°F, W %	2.8	7.8

(1) Cut feed was a 365°F$^+$ cut of the as-received crude phenol and amounted to 66.5 W % of the as-received crude phenol.

(2) The 365°F$^-$ cut of the as-received crude phenol was not analyzed.

TABLE 1. FEEDSTOCK ANALYSIS (Concluded)

MATERIAL	HRI No. 5511	L-731	Recycle(1)
DESCRIPTION	GPGP CRUDE PHENOL	CUT FEED	FROM RUN 60
GC Analysis Dry Basis, W %			
Benzene	0.1	0.0	0.0
Toluene	0.3	0.0	39.8
M-Xylene	0.2	0.1	2.0
Ethylbenzene	0.2	0.2	1.6
Phenol	45.9	19.8	2.8
o-Cresol	8.8	8.0	0.8
m-Cresol	13.9	19.9	19.6
p-Cresol	9.2	12.9	5.5
2-Ethylphenol(2)	0.9	1.1	0.2
3-Ethylphenol	1.5	2.1	1.2
4-Ethylphenol	1.8	2.5	0.6
2,3 & 3,5 Xylenol	2.6	3.6	0.0
2,4 & 2,5 Xylenol	2.5	6.1	0.0
2,6 Xylenol	0.6	0.8	0.6
3,4 Xylenol	3.7	5.6	0.0
Catechol	0.9	3.1	0.7
Resorcinol	0.0	0.3	1.0
Guaiacol	2.6	3.4	0.0
Pyridine	0.0	0.1	0.2
Lights	0.7	0.1	0.0
Heavies(3)	3.6	10.3	23.4
TOTAL	100.0	100.0	100.0

(1) The recycle material GC analysis was obtained by addition. Run 60's 375°F$^+$ liquid product was blended with known quantities of toluene, xylene and ethylbenzene. The GC analysis of the 375°F$^+$ material is presented in Table D-4.

(2) Includes hydroquinone.

(3) Heavies are defined as any unknown whch eluted after phenol did during the GC analysis. The disproportionate increase in heavies in the L-731 may be due to the atmospheric distillation of the as-received crude phenol.

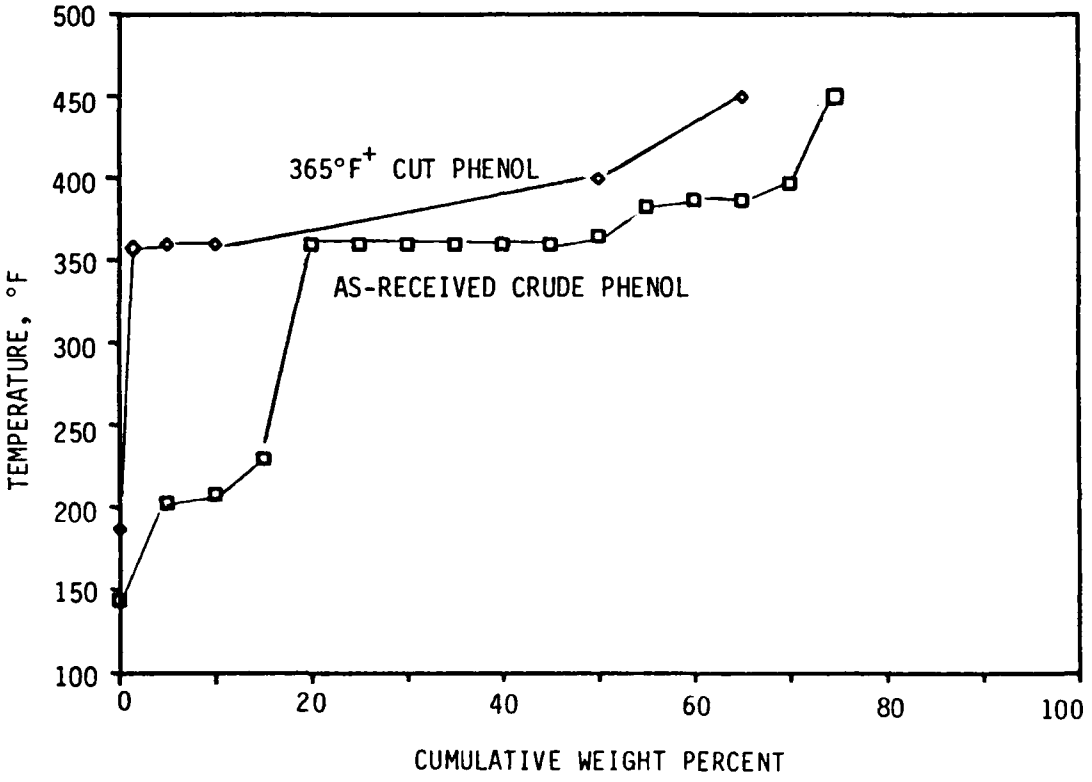


FIGURE 2. TBP DISTILLATIONS - AS-RECEIVED CRUDE AND CUT PHENOLS

TASK 2 - PROCESS VARIABLE STUDY

The purpose of Task 2 was to quantify the effect of several process variables on benzene and phenol yield using the Dynaphen bench unit described in Appendix B. Figure 3 is a schematic representation of the 2 operation modes utilized in the process variable study. In Runs 42-46, the as-received crude phenol was charged directly to the reactor with hydrogen. Subsequent runs utilized a 365°F$^+$ cut phenol feed and hydrogen as reactor feeds. The operating conditions used in these runs are summarized in Table 2.

Temperature was the primary process variable investigated during this program. Other process variables examined included initial feed phenol concentration, water dilution of the feed, pressure and residence time.

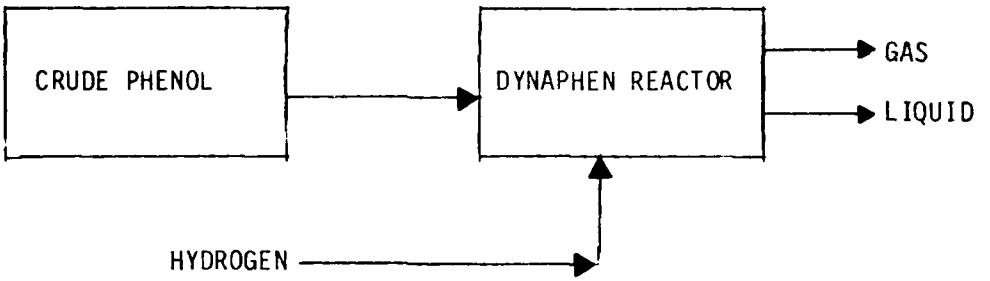
Appendix C contains the normalized yield results from this program. Liquid product inspections are presented in Appendix D. In the following discussions, yields will be expressed as weight percent of dry reactor feed unless otherwise stated.

Yields were normalized by taking the reactor liquid feed rate and composition, the unit vent gas rate and composition and the dry liquid product composition as correct. First, carbon was balanced by multiplying the flow rate of each carbon containing liquid product by a common factor so that the carbon fed to the unit equalled the combined carbon in the gas and liquid products. This common factor was defined by the division of the quantity of carbon in the feed less the carbon in the gas product by the carbon recovered in the liquid product. Oxygen was then balanced, assuming unaccounted oxygen was in the form of water. Sulfur was balanced, by saying that any sulfur from the feed not detected as hydrogen sulfide was in the liquid product. Nitrogen was balanced assuming any nitrogen not in the form of pyridine was in the liquid product. Lastly, the hydrogen in the feed was subtracted from the hydrogen in the products to get the hydrogen consumption rate. For normalization purposes unidentified lights were assumed to be methoxybenzene while unidentified heavies were assumed to be resorcinol.

In this program, residence time was always based on the total material going through the reactor, i.e., fresh feed, deionized water, hydrogen and recycle material.

Typically, material balance periods were 3 hours in duration and were preceded by a 2 hour at condition line-out period.

WHOLE FEED OPERATIONS



CUT FEED SINGLE PASS OPERATIONS

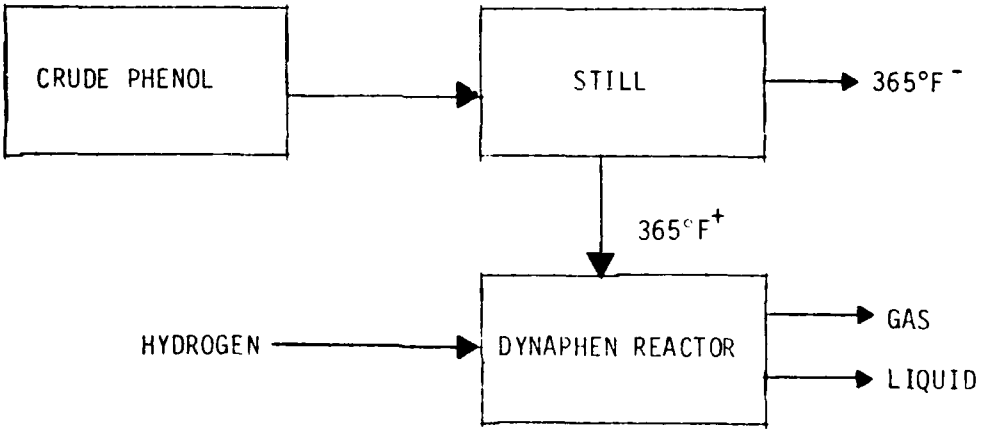


FIGURE 3. PROCESS VARIABLE STUDIES

TABLE 2. OPERATIONS SUMMARY

PROCESS VARIABLE STUDY OPERATIONS - WHOLE FEED

RUN NUMBER	FEED	PRESSURE, PSIG	RESIDENCE TIME, SEC.	REACTOR TEMPERATURE, °F	H_2 FEED RATE, SCFH(6)
237-42	HRI No. 5511(1)	600	29.2	1100	5.1
237-43	HRI No. 5511	600	29.0	1150	4.9
237-44	HRI No. 5511	600	28.8	1200	4.8
237-45	HRI No. 5511	600	28.7	1250	4.6
237-46	HRI No. 5511	600	28.5	1300	4.5

PROCESS VARIABLE STUDY OPERATIONS - CUT FEED

RUN NUMBER	FEED	PRESSURE, PSIG	RESIDENCE TIME, SEC.	REACTOR TEMPERATURE, °F	H_2 FEED RATE, SCFH(6)
237-47(2)	L-731 (3)	600	29.9	1140	4.6
237-48	L-731	600	29.7	1180	4.5
237-49	L-731	600	29.6	1220	4.4
237-50	L-731/H_2O	600	27.8	1220	4.3
237-51	L-731/H_2O	600	27.7	1260	4.2
237-52	L-731/H_2O	600	27.6	1300	4.1
237-53	L-731/H_2O	900	29.7	1260	6.2
237-54	L-731/H_2O	600	46.3	1260	2.1

CONTINUOUS ONCE THROUGH TEST - CUT FEED

RUN NUMBER	FEED	PRESSURE, PSIG	RESIDENCE TIME, SEC.	REACTOR TEMPERATURE, °F	H_2 FEED RATE, SCFH(6)
237-60(4)	L-731/H_2O	600	27.3	1260	4.2

DEMONSTRATION TEST - CUT FEED

RUN NUMBER	FEED	PRESSURE, PSIG	RESIDENCE TIME, SEC.	REACTOR TEMPERATURE, °F	H_2 FEED RATE, SCFH(6)
237-61(5)	L-731/H_2O and Recycle	600	27.7	1260	4.2

(1) HRI No. 5511 is the as-received crude phenol from ANG.
(2) Runs 50 through 54 were with 8 W % water and 92 W % L-731.
(3) L-731 is a nominal 365°F$^+$ cut of the crude phenol stream.
(4) Run 60 was with 10 W % water and 90 W % L-731.
(5) Run 61 was with 10.0 W % water, 74.9 W % L-731 and 15.1 W % recycled material.
(6) Make-up hydrogen purity was 99+ percent.

Temperature Effect

Two temperature studies were conducted as part of the process variable study. The first study utilized the as-received crude phenol material while the later study was with the nominal 365°F$^+$ cut of the crude phenol. Increasing reactor temperature had a large effect on the product slates.

A series of five different operations (Runs 42-46) were conducted at various temperatures, ranging from 1100°F to 1300°F with the as-received crude phenol. All operations with the as-received phenol indicated a negative phenol production. Additional operations were then performed with a cut feed in a successful demonstration of net phenol make, examining five temperatures, ranging from 1140°F to 1300°F. Initially, water was not added to the cut phenol. However, operating problems did arise with the reactor feed line plugging after about six hours of operation with dry cut phenol feed during Runs 47-49. The cause of feed line plugging was not investigated but may have been due to either coking or polymerization reactions. The remainder of the process variable study utilized a reactor feed of 8 W % deionized water and 92 W % cut phenol.

All temperature study operations were carried out at 600 psig and a nominal 30 second residence time. The results of these studies are shown in Tables 3 and 4 and Figures 4-15.

- Crude Phenol Study - Runs 42-46 - Benzene yield increased steadily from 1.2 W % to 35.9 W % with increasing temperature. Phenol yield decreased steadily from 43.3 W % to 20.2 W % as temperature was increased.

  Cresylic acid yields decreased as they were increasingly consumed with increasing reactor severity. The total cresylic acid yield ranged from 39.6 W % at 1100°F to 1.4 W % at 1300°F.

  Toluene yields increased with increasing temperature to 6.6 W % at 1250°F then decreased to 4.0 W % at 1300°F as toluene was increasingly converted to benzene. Xylene and ethylbenzene yields were small throughout these 5 experiments.

Gas yields steadily increased from 7.6 W % to 29.1 W % with increasing temperature. Maximum methane and C_2 gas yields were achieved at the highest temperature tested. C_3 gas yields increased to 2.4 W % as reactor temperature was increased to 1200°F, then decreased with subsequent increases in severity.

Carbon monoxide yield increased from 2.7 W % to 7.5 W % with increasing temperature. Carbon dioxide yields from these runs were less than 0.5 W % of the reactor feed.

Hydrogen consumption increased with increasing temperature from 0.5 W % at 1100°F to 3.7 W % at 1300°F.

- Cut Phenol Study - Runs 47-52 - Benzene yield increased from 1.3 W % to 42.1 W % with increasing temperature. Phenol yield increased from 22.4 W % to 29.9 W % as the reactor temperature was increased to 1220°F. Further temperature increases, lowered the phenol yield, to 26.5 W % and then 12.9 W % at 1300°F.

  Cresylic acid yields were similar to the whole crude results, decreasing as they were increasingly consumed with increasing reactor temperature. The total cresylic acid yield decreased from an initial 46.2 W % to 1.6 W % with increasing temperature.

  Toluene yields increased with increasing temperature to 8.7 W % at 1260°F then decreased to 3.8 W % at 1300°F as toluene was increasingly converted to benzene. Xylene and ethylbenzene yields again were 1.0 W % or less throughout these experiments.

  Gas yields steadily increased from 19.2 W % to 26.2 W %. Maximum methane and C_2 gas yields were achieved at the highest temperature tested. C_3 gas yields increased to 2.4 W % as reactor temperature was increased to 1180°F, then decreased with subsequent increases in severity.

  Carbon monoxide yield was between 6.9 and 7.5 W % throughout these tests. Carbon dioxide yields from these runs were less than 0.5 W % of the reactor feed.

  As expected, hydrogen consumption again increased with increasing temperature, from 1.2 W % at 1140°F to 3.3 W % at 1300°F.

- Adjusted Total Yields - In order to assess the benefit of removing phenol from the as-received crude phenol, the distillation overhead phenol content was added to the cut phenol Dynaphen yields by the following calculation. This makes it easier to compare the cut phenol results with the crude phenol results. Figure 16 is a schematic representation of this calculation, showing the as-received feed being distilled before Dynaphen processing of the heavier fraction. Total benzene and phenol yields were then calculated and are presented in Figures 17. The calculation method for benzene and phenol on a dry basis was:

  Total Yield = Dynaphen Yield + Overhead Content

  $$\text{Dynaphen Yield} = \text{Cut Feed Dynaphen Yield} \times \frac{\text{dry cut feed}}{\text{dry crude}}$$

  Dynaphen Yield = Cut Feed Dynaphen Yield x (0.665/0.9504)

  Overhead Content = Dry Crude Content - Cut Crude Content

  Overhead Content = 45.9 - 19.8 x (0.665/0.9504) = 32.0 W %

  In this analysis, the benzene content in the distillation overhead stream was assumed to be zero. Total benzene plus phenol yields increased from 47.6 W % at 1140°F to 70.4 W % of the dry crude phenol at 1300°F.

TABLE 3. PROCESS VARIABLE STUDY - WHOLE CRUDE PHENOL RESULTS

Gas Yields and Hydrogen Consumption, W % Dry Reactor Feed

Run	C_1	C_2	C_3	CO	CO_2	Total Gas	Hydrogen Consumption
42	1.6	1.1	1.0	2.7	0.1	7.6	0.5
43	3.6	2.2	1.9	4.2	0.3	13.6	1.1
44	7.0	4.0	2.4	6.7	0.2	20.9	1.9
45	10.2	5.8	1.4	7.3	0.4	25.1	2.7
46	13.2	7.3	0.7	7.5	0.4	29.1	3.7

Liquid Yields, W % Dry Reactor Feed

Run	Benzene	Phenol	Cresol	Xylenol	Ethyl-Phenol	Toluene	Xylene	Ethyl-Benzene
42	1.2	43.3	29.2	6.5	3.9	1.6	0.4	0.5
43	2.4	42.9	25.6	4.4	3.2	2.8	0.5	0.8
44	6.4	41.1	18.3	2.2	1.8	4.8	0.6	1.0
45	16.6	36.8	8.1	0.7	0.5	6.6	0.4	0.6
46	35.9	20.2	1.2	0.2	0.0	4.0	0.1	0.2

TABLE 4. PROCESS VARIABLE STUDY - CUT CRUDE PHENOL RESULTS

Gas Yields and Hydrogen Consumption, W % Dry Reactor Feed

Run	C_1	C_2	C_3	CO	CO_2	Total Gas	Hydrogen Consumption
47	4.3	2.8	2.2	7.5	0.2	19.2	1.2
48	6.2	4.6	2.4	7.1	0.4	21.6	1.9
49	7.0	5.1	2.0	7.0	0.3	22.0	2.0
50	6.4	4.8	2.1	6.9	0.3	21.0	1.8
51	9.7	6.8	1.2	7.2	0.4	25.5	2.7
52	10.9	7.8	0.3	6.9	0.3	26.2	3.3
53	9.9	6.9	1.3	7.3	0.4	25.9	2.9
54	11.0	6.7	0.2	6.2	0.4	24.6	3.3

Liquid Yields, W % Dry Reactor Feed

Run	Benzene	Phenol	Cresol	Xylenol	Ethyl-Phenol	Toluene	Xylene	Ethyl-Benzene
47	1.3	22.4	34.1	7.4	4.7	3.2	0.5	0.6
48	4.0	26.3	26.6	4.1	2.8	6.2	0.9	1 0
49	8.0	29.9	20.1	2.1	1.4	8.3	0.8	0.9
50	6.5	29.8	22.4	2.9	1.9	7.3	0.8	0.9
51	19.1	26.5	7.8	1.1	0.6	8.7	0.4	0.5
52	42.1	12.9	0.9	0.4	0.3	3.8	0.1	0.1
53	28.0	22.9	4.1	0.6	0.3	7.4	0.2	0.3
54	41.2	14.9	1.1	0.3	0.2	4.4	0.1	0.1

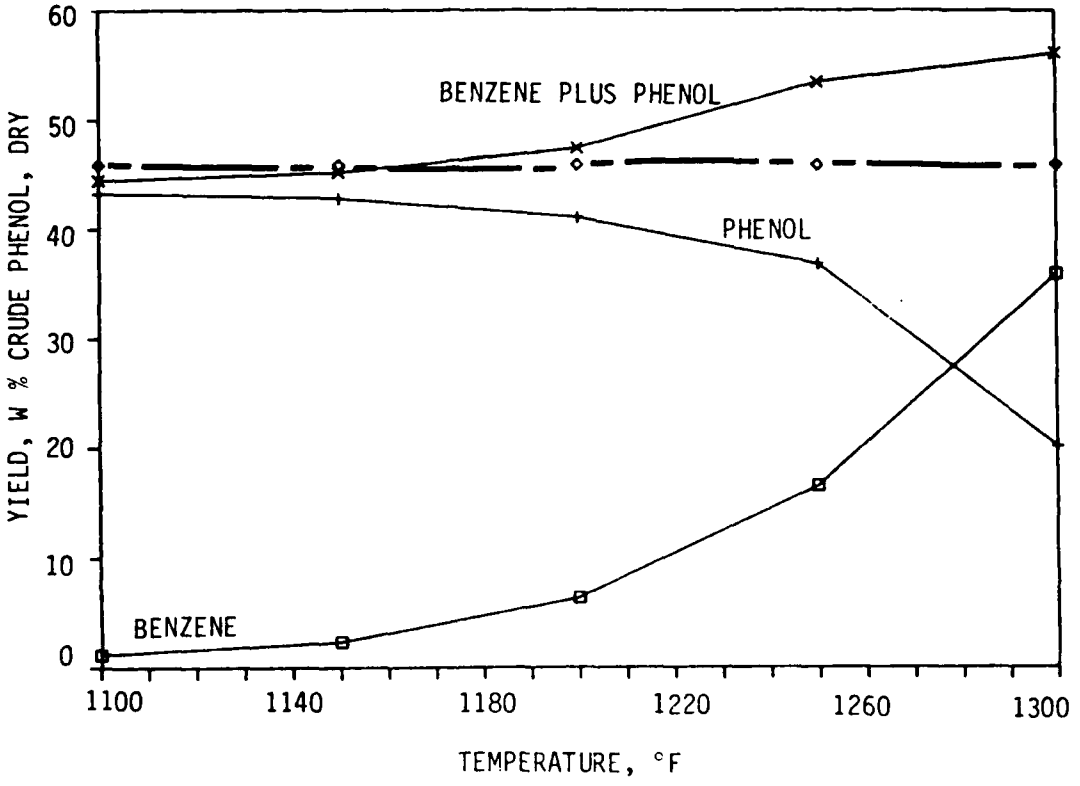


FIGURE 4. GPGP CRUDE PHENOL RESULTS - BENZENE AND PHENOL YIELDS

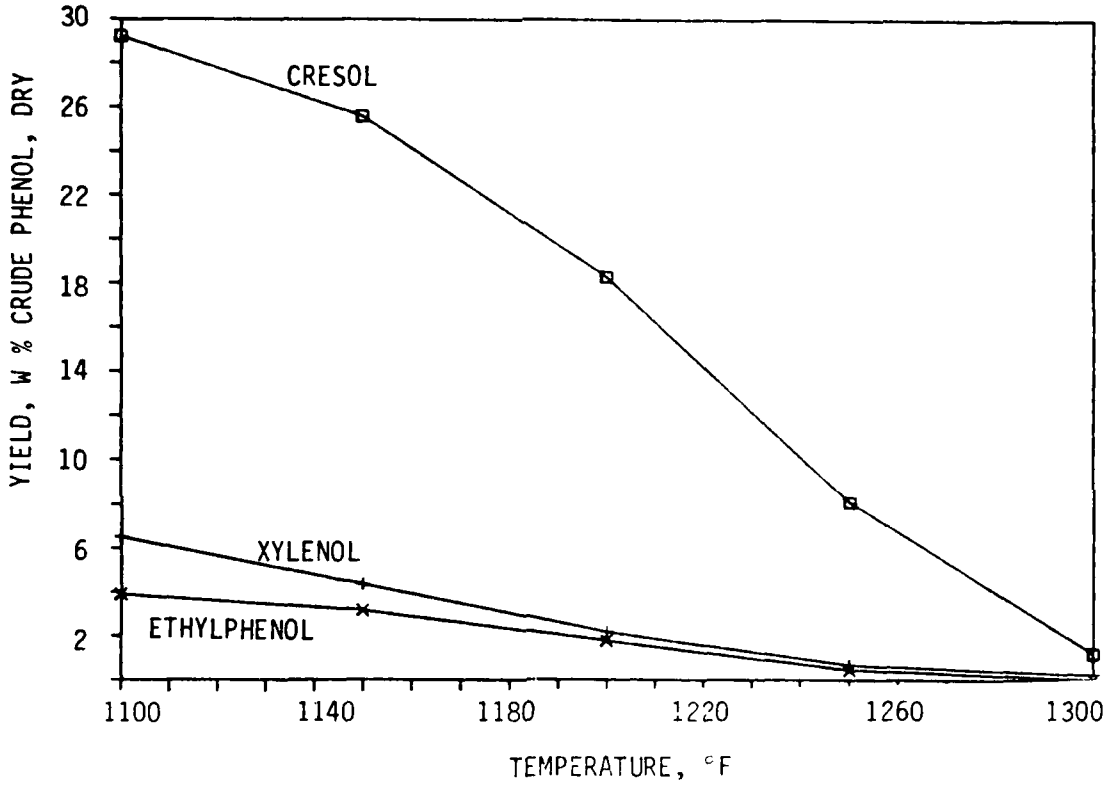


FIGURE 5. GPGP CRUDE PHENOL RESULTS - CRESOL, XYLENOL AND ETHYLPHENOL

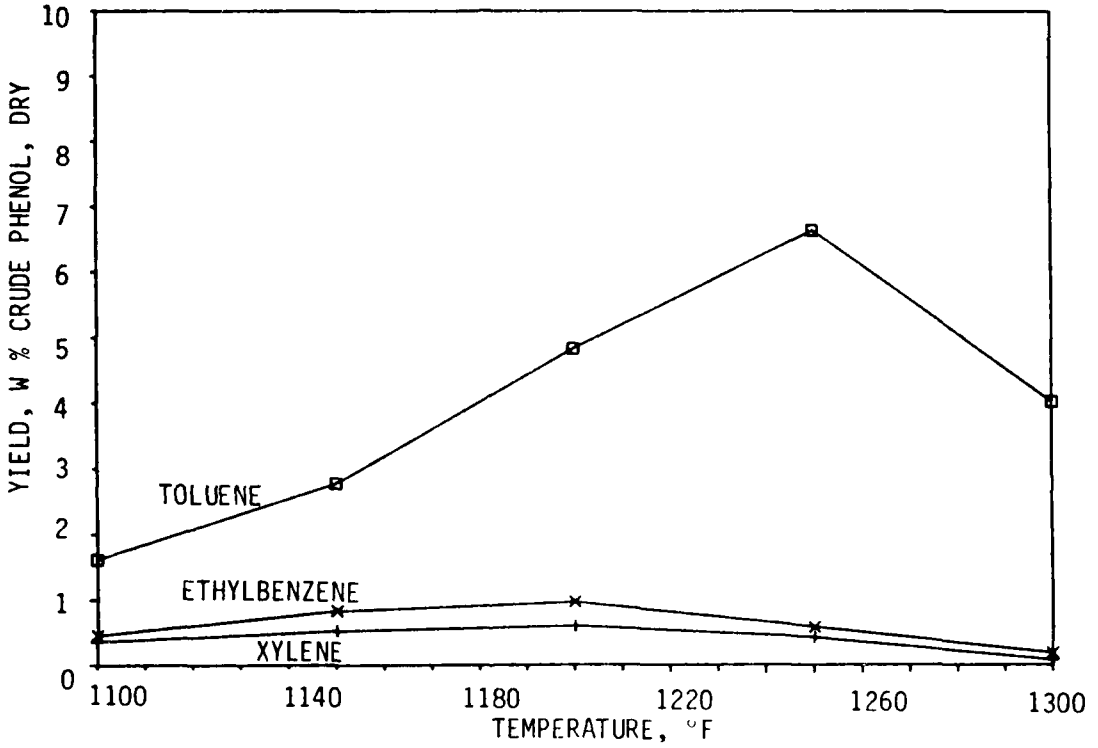


FIGURE 6. GPGP CRUDE PHENOL RESULTS - TOLUENE, XYLENE AND ETHYLBENZENE

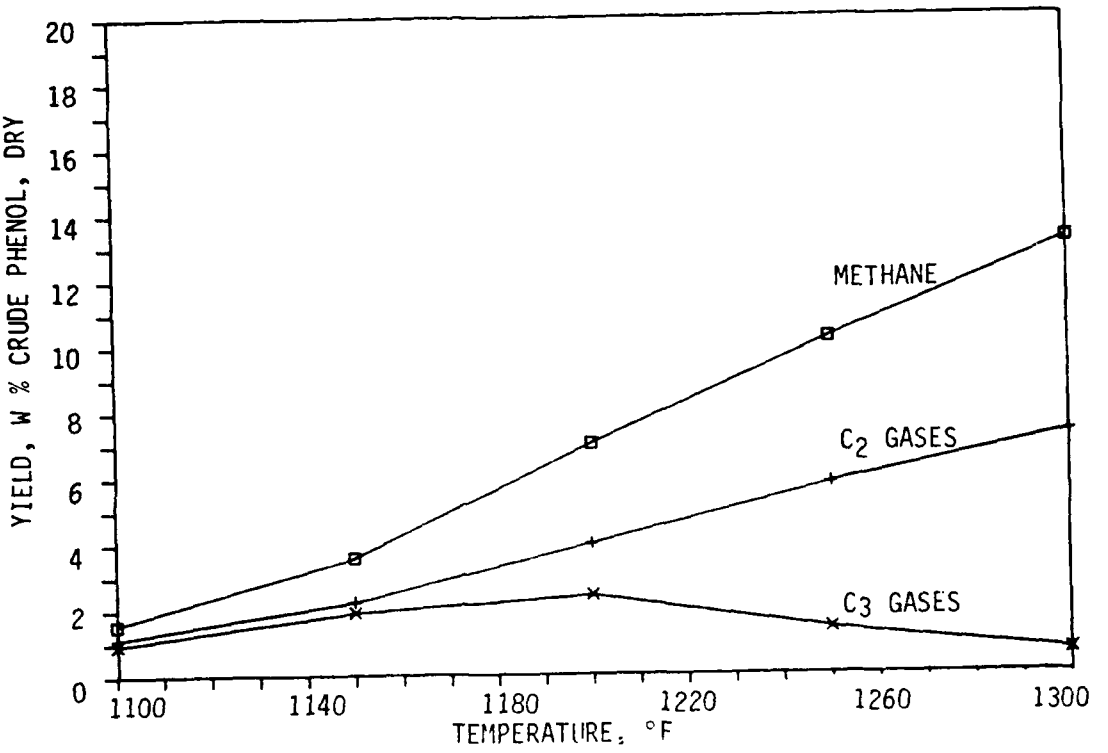


FIGURE 7. GPGP CRUDE PHENOL RESULTS - C_1 TO C_3 GAS YIELDS

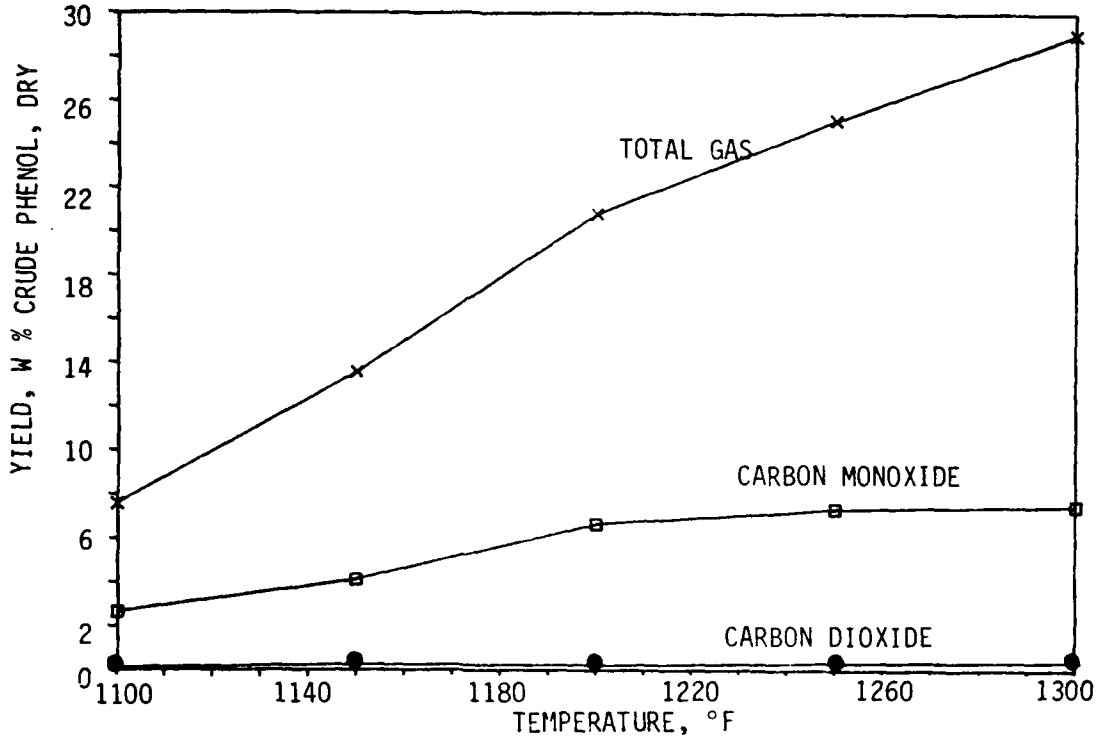


FIGURE 8. GPGP CRUDE PHENOL RESULTS - CO, CO_2 AND TOTAL GAS YIELD

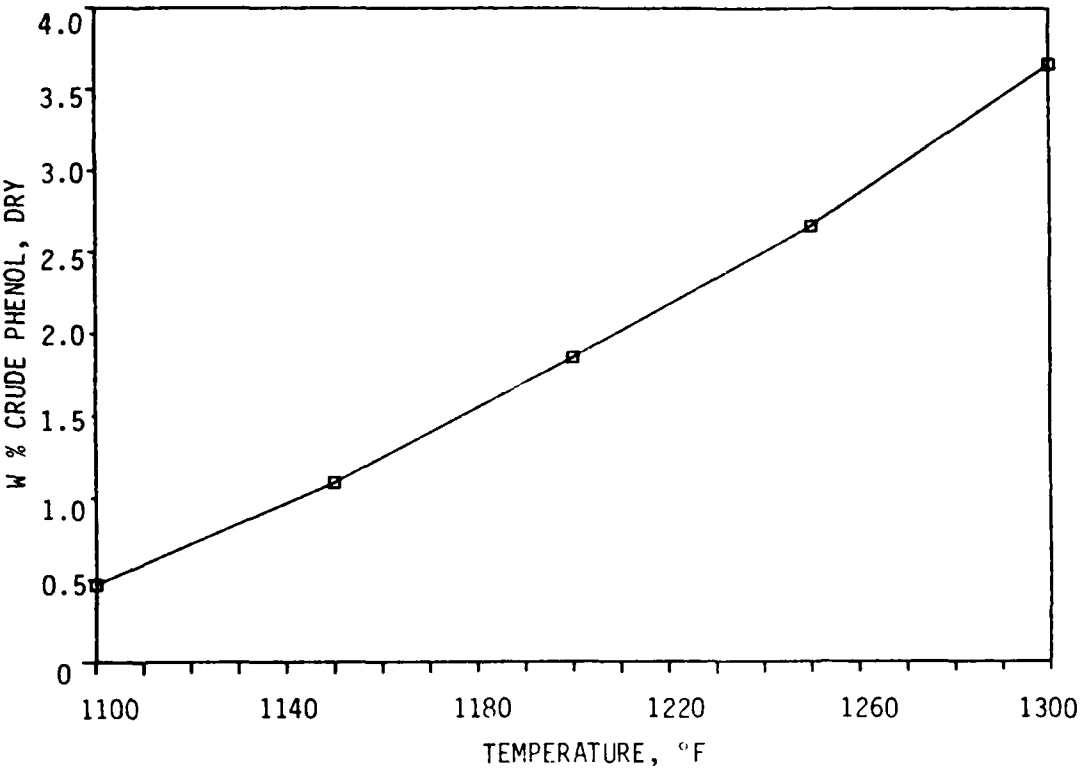
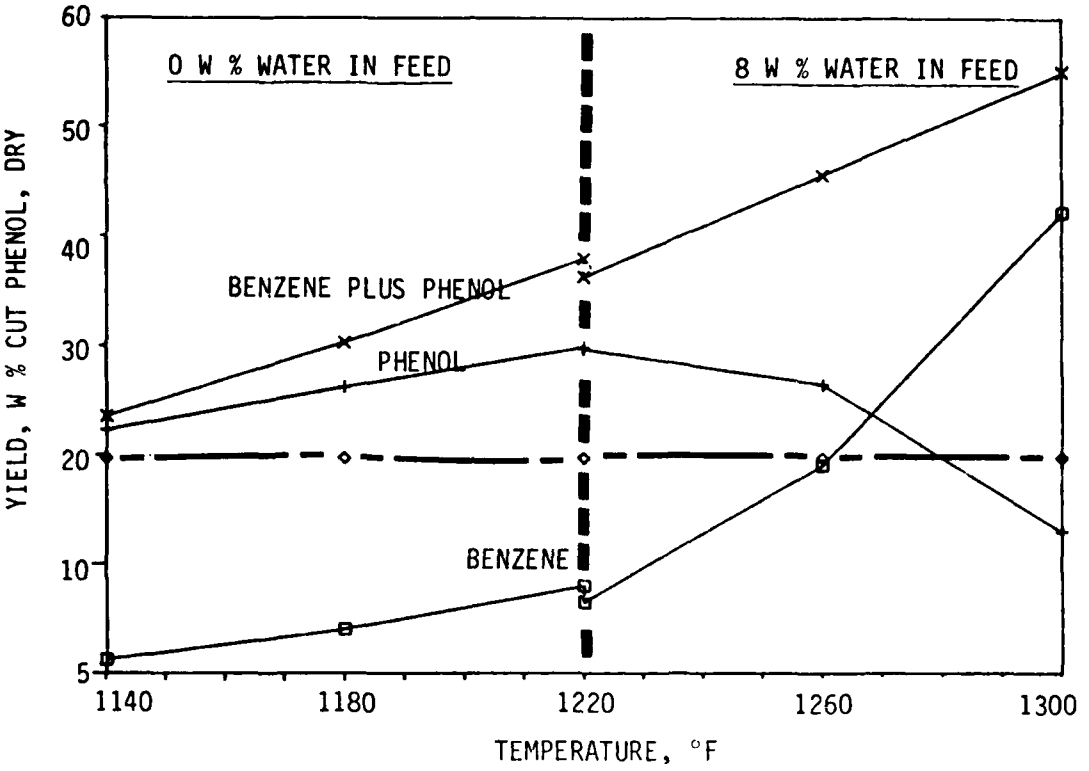


FIGURE 9. GPGP CRUDE PHENOL RESULTS - HYDROGEN CONSUMPTION



◇ ——— — — Phenol concentration in cut phenol.

PHENOL YIELDS AT 1220°F	
Dry Feed	29.90 W %
Wet Feed	29.77 W % on a dry basis

FIGURE 10. GPGP CUT PHENOL RESULTS - BENZENE AND PHENOL YIELDS

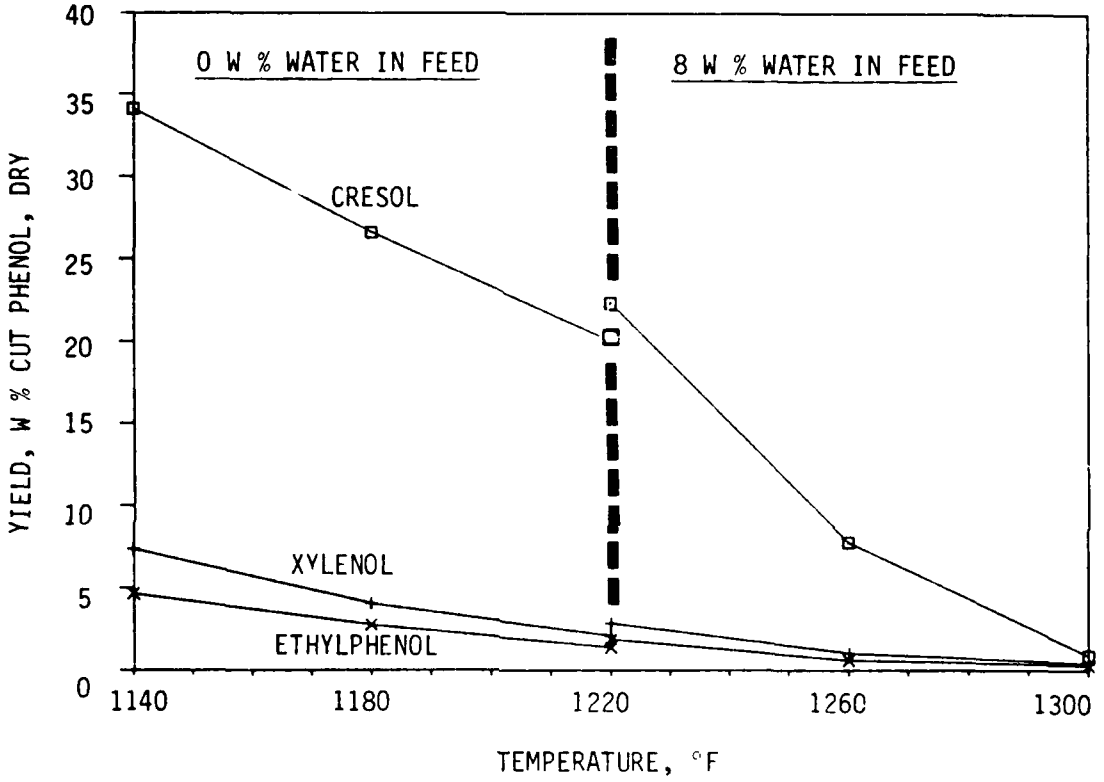


FIGURE 11. GPGP CUT PHENOL RESULTS - CRESOL, XYLENOL AND ETHYLPHENOL

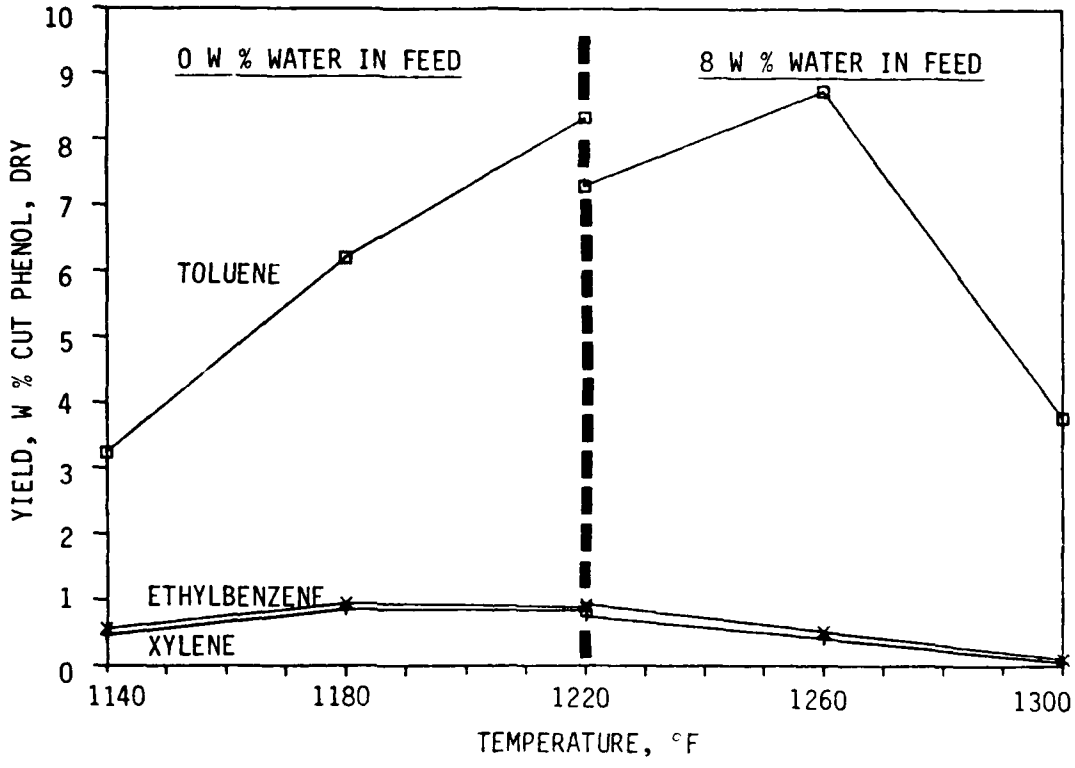


FIGURE 12. GPGP CUT PHENOL RESULTS - TOLUENE, XYLENE AND ETHYLBENZENE

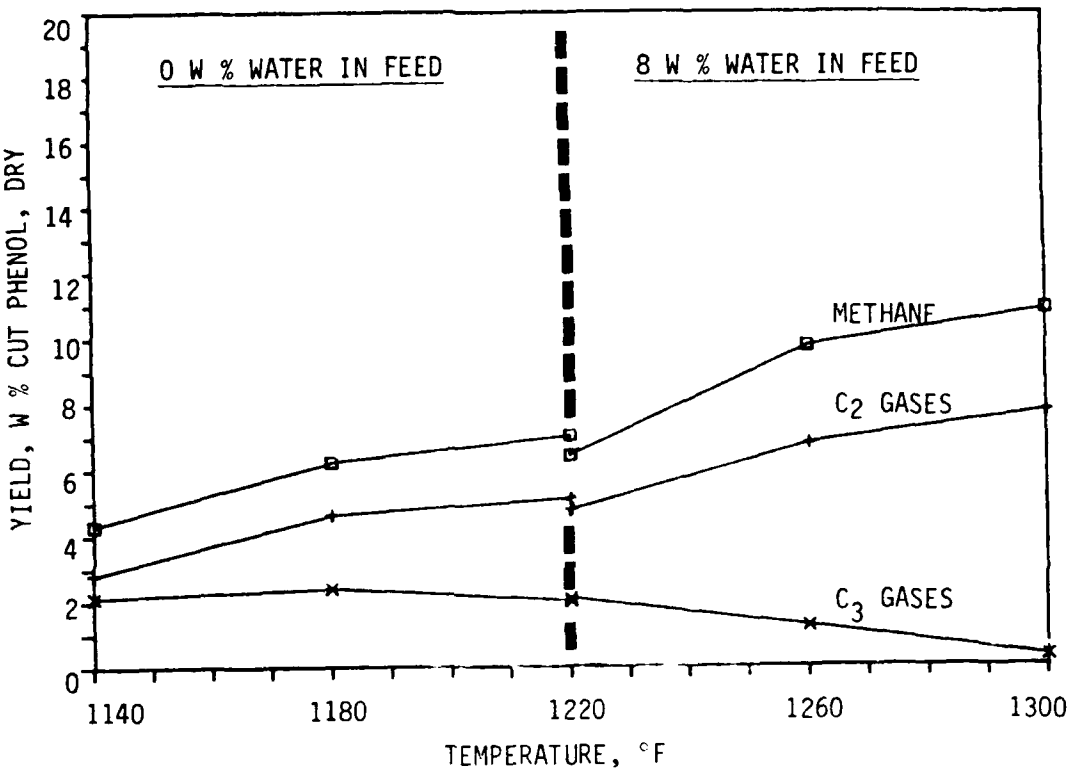


FIGURE 13. GPGP CUT PHENOL RESULTS - C_1-C_3 GAS YIELDS

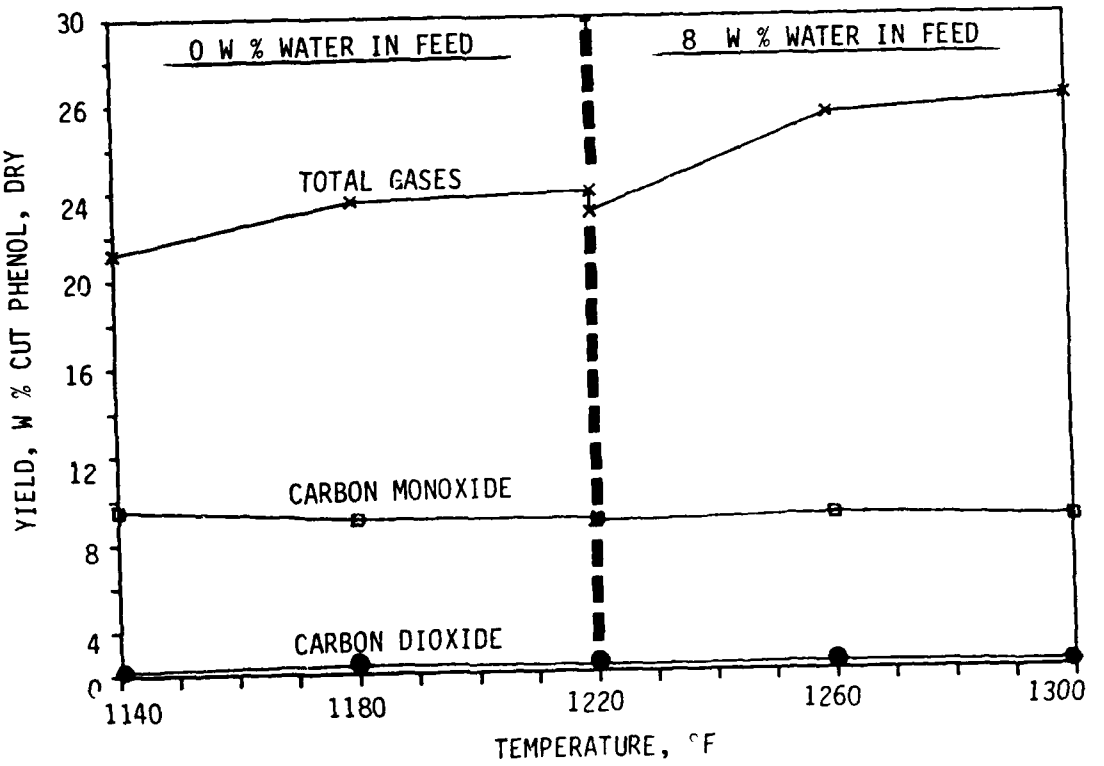


FIGURE 14. GPGP CUT PHENOL RESULTS - CO, CO_2 AND TOTAL GAS YIELD

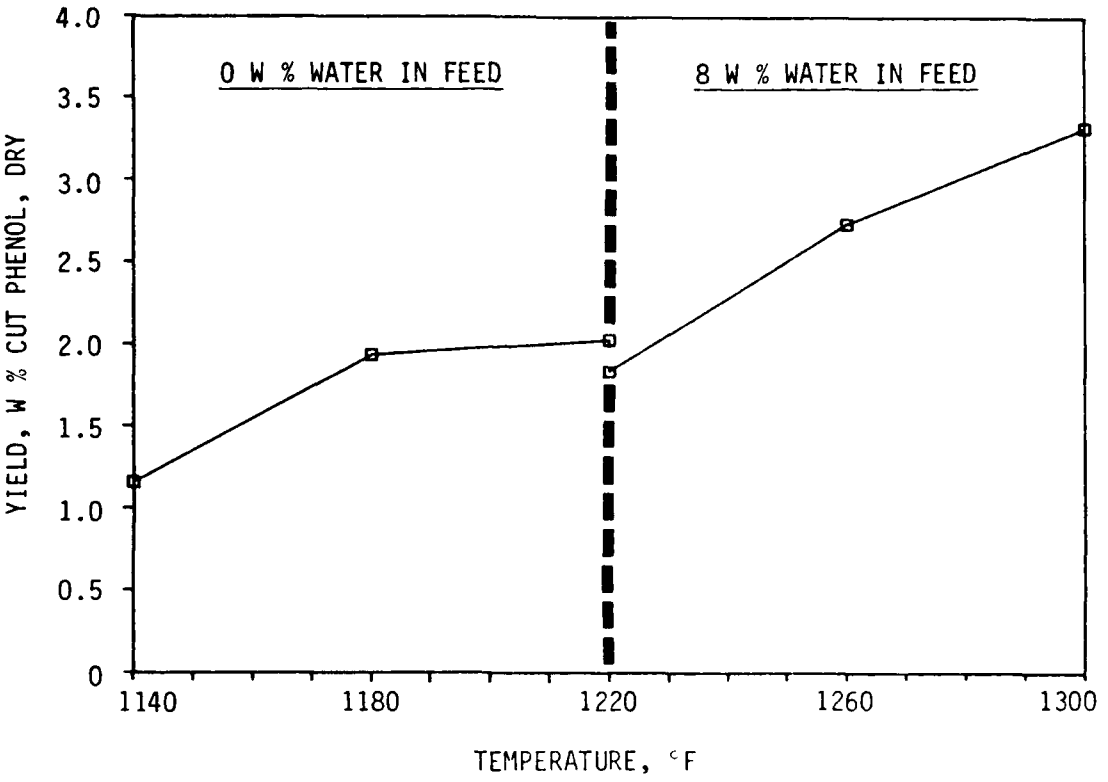
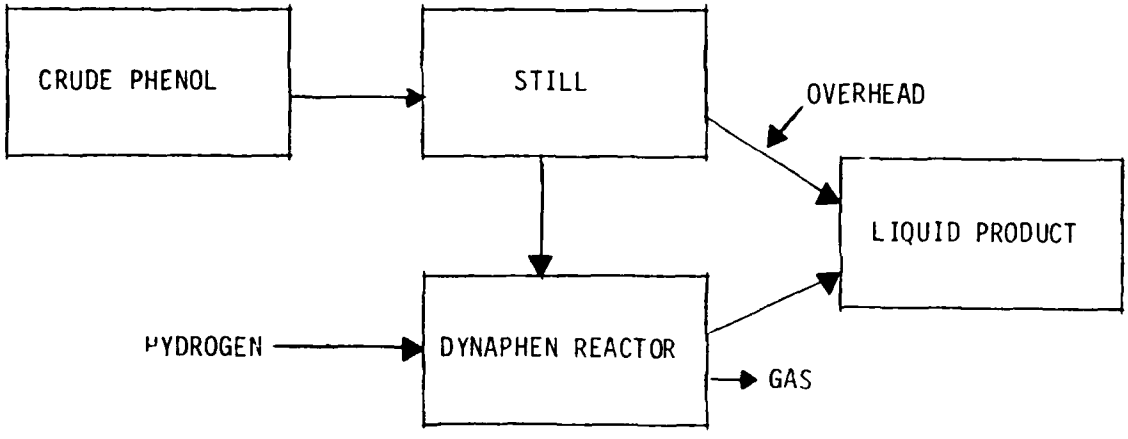


FIGURE 15. GPGP CUT PHENOL RESULTS - HYDROGEN CONSUMPTION



NOTE:
A nitrogen purge was used during the distillation of the crude phenol. Any gas which may have evolved during the distillation would have been flared with the nitrogen without detection.

FIGURE 16. DISTILLATION PLUS DYNAPHEN - LIQUID PRODUCT

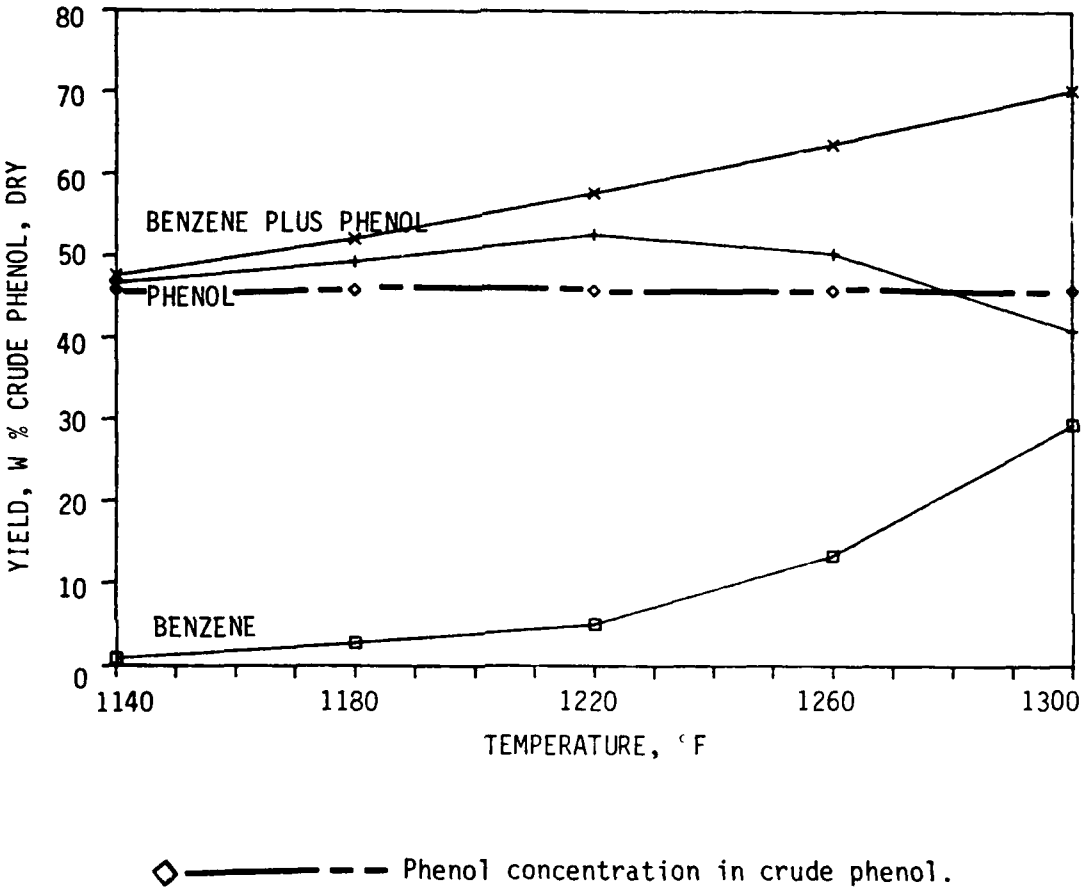


FIGURE 17. DISTILLATION PLUS DYNAPHEN - BENZENE AND PHENOL YIELDS

Initial Phenol Concentration Effect

The as-received feedstock contained 45.9 W % phenol and 31.9 W % cresol while the 365°F$^+$ cut contained 19.8 W % phenol and 40.8 W % cresol (refer to Task 1 for additional information).

As shown in Figures 4 and 10, the lower phenol concentration and higher cresol concentration in the 365°F$^+$ cut produced a different benzene and phenol yield than the whole crude produced. In every operation with the crude phenol feedstock, net phenol make was negative. Conversely, in five of the six operations with the cut phenol feedstock, net phenol make was positive. At 1220°F, the increase in phenol was more than 50% (29.9 W %/19.8 W %).

These results indicate Dynaphen can either be utilized to increase phenol yields with benzene as a second product or be used to produce solely benzene from GPGP crude phenol.

Increased phenol yields can be achieved by first lowering the phenol concentration in the reactor feed to below 20 W % and then reacting the cut phenol with hydrogen at temperatures below 1280°F.

Maximum benzene yields can be achieved at operating conditions which are slightly more severe than Run 46, completely converting all of the phenolic compounds to benzene.

In this study, 1260°F, 600 psig and 30 seconds residence time were chosen for the continuous once through test rather the 1220°F because the 12.6 W % increase in benzene yield was thought to more than offset the 3.3 W % decrease in phenol yield. The higher conversion level would also reduce the recycle requirements of a commercial facility.

Water Effect

A previous study[3] indicated process selectivity to phenol can be increased by adding water to the reactor feed. In the prior study, water to feed molar ratios were between two and five, whereas the current program dealt with water to feed molar ratios between 0 and 0.65.

Three experiments were made with dry cut phenol feed. In each of these operations, the reactor feed line plugged after about six

hours of dry cut phenol feed. Subsequent tests were performed with 8 W % water added to the cut phenol feed. This improved unit operation and the allowed the program to be completed.

Comparing the yields and hydrogen consumption data presented in Figures 10-15, low concentrations of water did not appear to have a large effect on the yield slate. Water improved the operation by acting as diluent and vapor pressure reducer of the components which caused the feed line plugging. Identification of these components and their preferential removal might eliminate the need for water addition.

Pressure Effect

An experiment was conducted at 900 psig instead of 600 psig to quantify the effect of pressure on this reaction system. For a single gas phase reaction like the one shown below, this pressure change should increase the rate of reaction by 220% if all of the other process variables are constant.

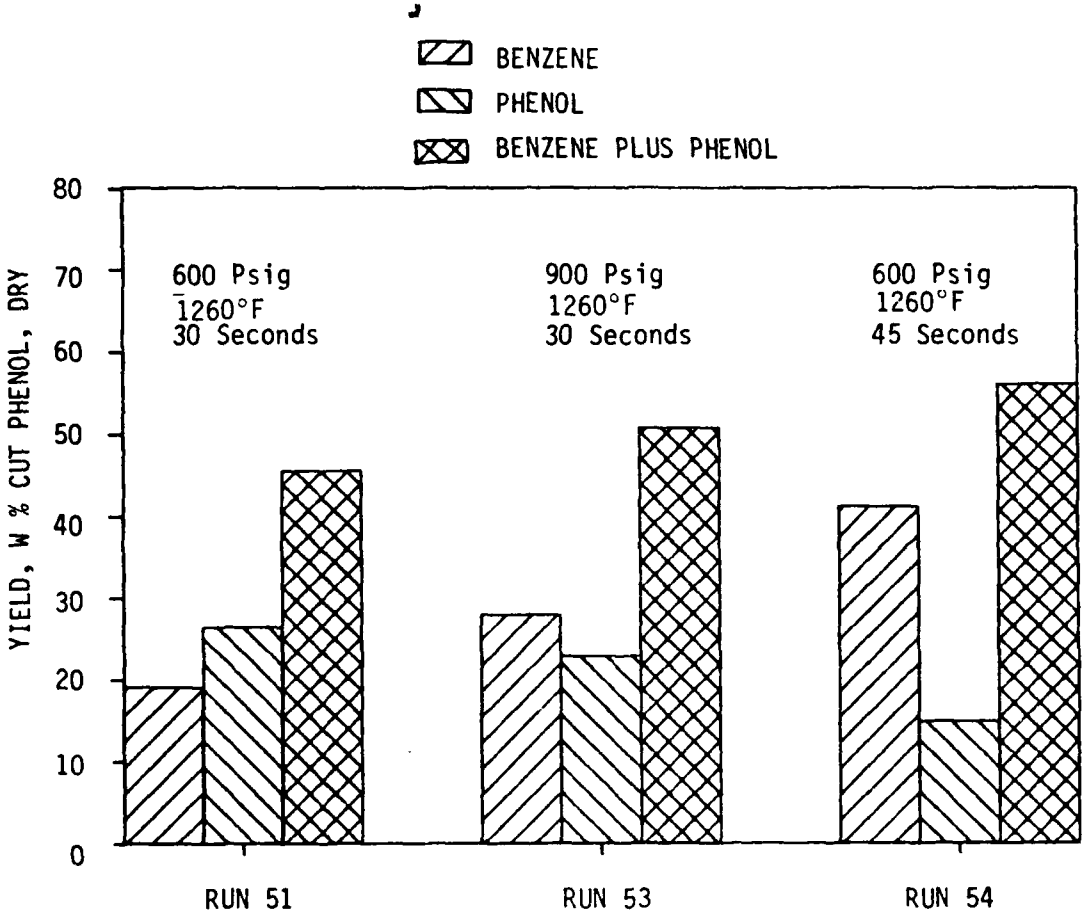
$$A + B \Rightarrow C + D$$

$$r = k[A][B] = k(Pa/RT)(Pb/RT) = kYaYb(P/RT)^{**}2$$

$$r2/r1 = (P2/P1)^{**}2 = (915/615)^{**}2 = 2.2$$

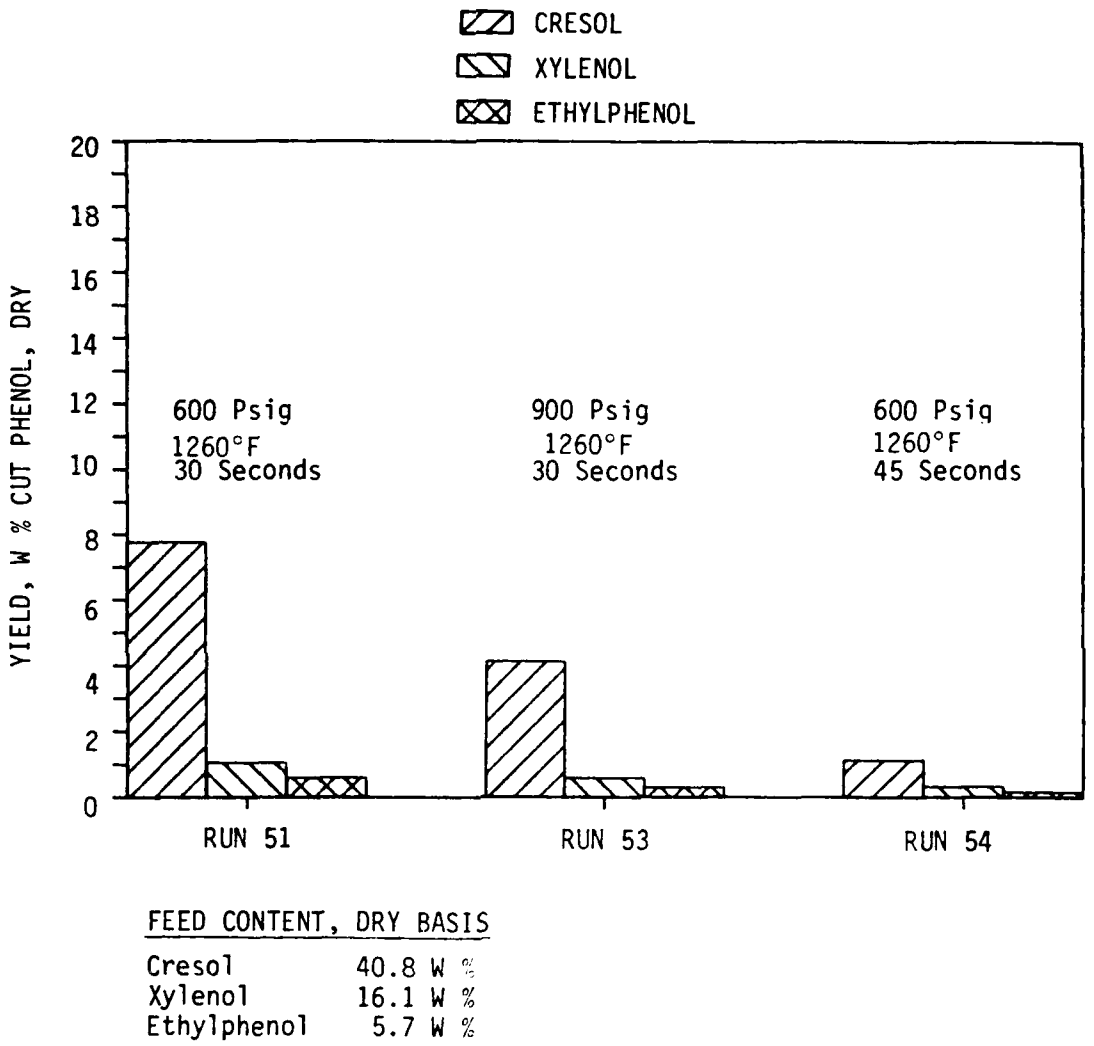
There are at least thirty simultaneous reactions occurring in the Dynaphen processing of GPGP crude/cut phenol, refer to Appendix A. As a result, the increase in benzene yield expected with GPGP crude/cut phenol is not immediately obvious.

Quantitative analysis of the phenol and benzene yields from Runs 51 (600 psig) and 53 (900 psig) are as one would expect. The higher pressure run had a 47% increase in benzene and lower yields of the other principal liquid components including phenol, refer to Table 4 and Figures 18-20. Net water yield was also higher, by 30 W %. Run 51's gas analysis was used in place of Run 53's gas analysis for computational purposes because of a bad gas sample. Gas yields between Runs 51 and 53, therefore, should not be compared.



FEED CONTENT, DRY BASIS	
Phenol	19.8 W %
Benzene	0.0 W %

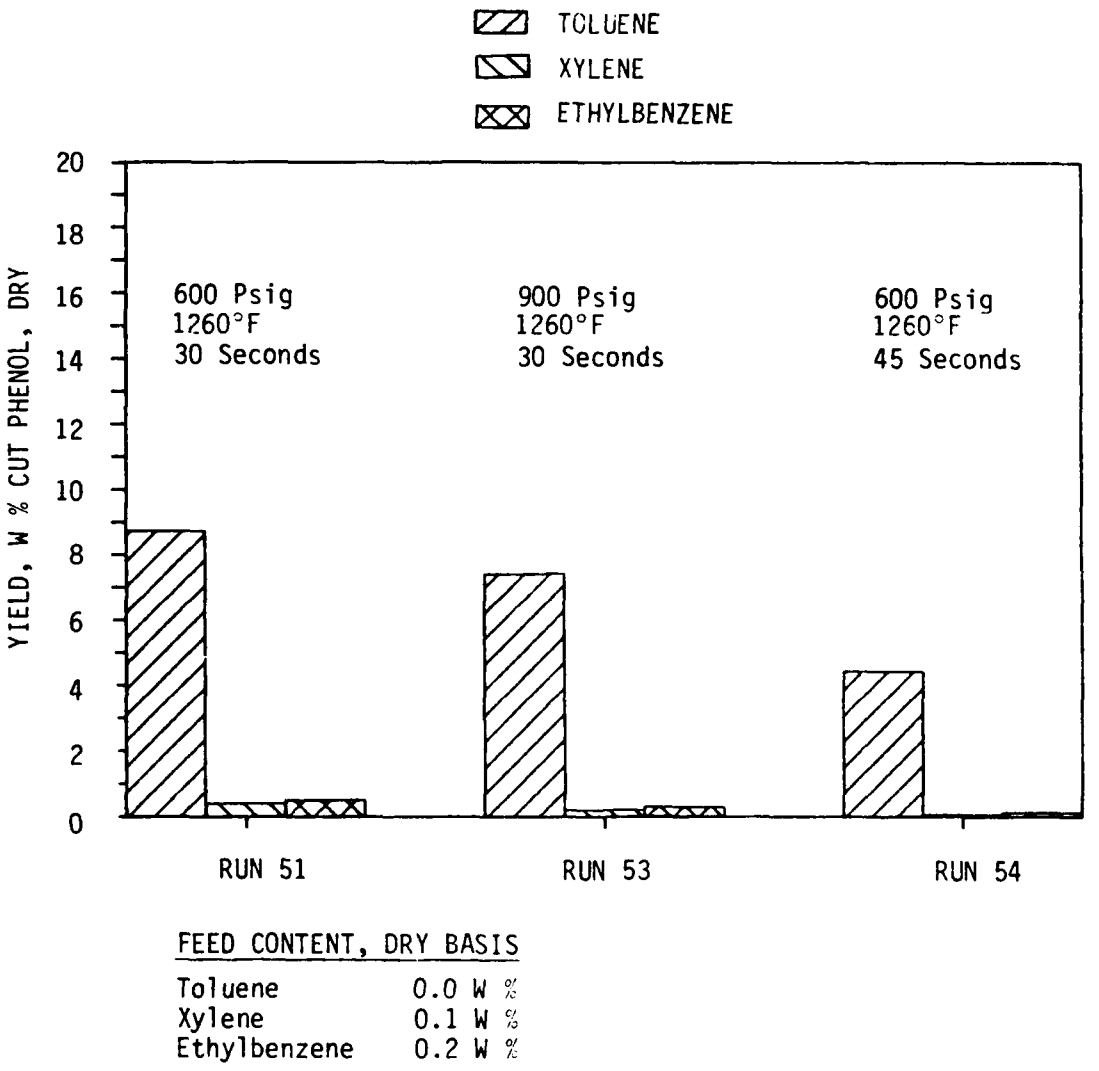
FIGURE 18. PRESSURE AND RESIDENCE TIME STUDY - BENZENE AND PHENOL YIELDS



FEED CONTENT, DRY BASIS

Cresol	40.8 W %
Xylenol	16.1 W %
Ethylphenol	5.7 W %

FIGURE 19. PRESSURE AND RESIDENCE TIME STUDY - CRESOL, XYLENOL AND ETHYLPHENOL



FEED CONTENT, DRY BASIS

Toluene	0.0 W %
Xylene	0.1 W %
Ethylbenzene	0.2 W %

FIGURE 20. PRESSURE AND RESIDENCE TIME STUDY - TOLUENE, XYLENE AND ETHYLBENZENE

Residence Time

An experiment was conducted to quantify the affect of residence time. Run 54 was performed with a residence time of 46.3 seconds, or 67% longer than Run 51. An increase in benzene yield was expected due to the longer residence time. A 216% increase in benzene yield was obtained, phenol and toluene yields were both nearly cut in half by the longer residence time. The other liquid reactants were nearly consumed. Increasing the reaction severity, increased water yield 31.6%. Total gas yield was slightly less with the longer reaction time, although methane yield did increase by 13%.

Refer to Table 4, Figures 18-20, Appendix C and Appendix D for additional details.

Lower benzene yields should result from lower residence time experiments. As residence times are reduced, less phenol is produced and less phenol is converted to benzene. The net effects of lower residence times on phenol yield is indeterminate without a detailed kinetic model or experimental data.

TASK 3 - CONTINUOUS ONCE-THROUGH TEST

The operating conditions selected for the continuous once-through test were:

Temperature	1260°F
Pressure	600 psig
Nominal Residence Time	30 seconds
Water Dilution	10 W % of Reactor Liquid Feed
Phenolic Feed	Cut Phenol, L-731

These conditions were similar to Run 51 which met the following criteria for the continuous once-through test.

- Significant positive net phenol yield.
- Significant benzene yield.
- As close as practical to commercial HDA conditions to minimize recycle scale-up difficulties, and investment costs.

Net phenol yield in Run 51 was 26.5 W % of the reactor feed or a 33.8% increase above the amount of phenol in the reactor feed. Benzene yield was 19.1 W %. These yields accounted for 63.9 W % of the dry liquid yields.

Figure 21 is a schematic representation of the continuous once-through operation. The as-received crude phenol was first distilled and the 365°F$^+$ cut was then charged to the Dynaphen reactor with hydrogen and water. The liquid product was then sent to another still to recover the 375°F$^+$ portion of the liquid product which was utilized as recycle material in the demonstration recycle run.

Normalized yield results for the continuous once-through test, Run 60, are presented in Table 5. Phenol yield was 24.5 W %, a 24% increase above the amount of phenol in the reactor feed. Benzene yield was 24.4 W %. Total cresol, xylenol and ethylphenol yield was 6.6 W % while the sum of the toluene, xylene and ethylbenzene yields was 9.5 W %.

Benzene yield from the continuous once-through test was higher than Run 51 of the process variable study, 24.4 W % compared to

19.1 W %. Conversely, phenol yield was slightly lower in the continuous once-through test, 24.5 W % compared to 26.5 W %, indicating more of the phenol was converted to benzene in this operation. Cresylic acid and the alkylbenzene yields also indicate the reaction progressed farther toward completion in Run 60 than it did in Run 51.

These liquid yields are also presented in Figures 22 to 24. Yields are expressed on a weight percent dry crude phenol basis with the calculated amount of phenol in the distillation overhead added to the Dynaphen phenol yield, as was previously done with Figure 17.

Gas yields from the continuous once-through test are also presented in Table 5. Each gas yield was slightly lower in the continuous once-through test than it was in Run 51. Total gas yields were 25.5 W % in Run 51 and 23.1 W % in the continuous once-through test.

Hydrogen consumption in the continuous test and in Run 51 was the same, 2.7 W %.

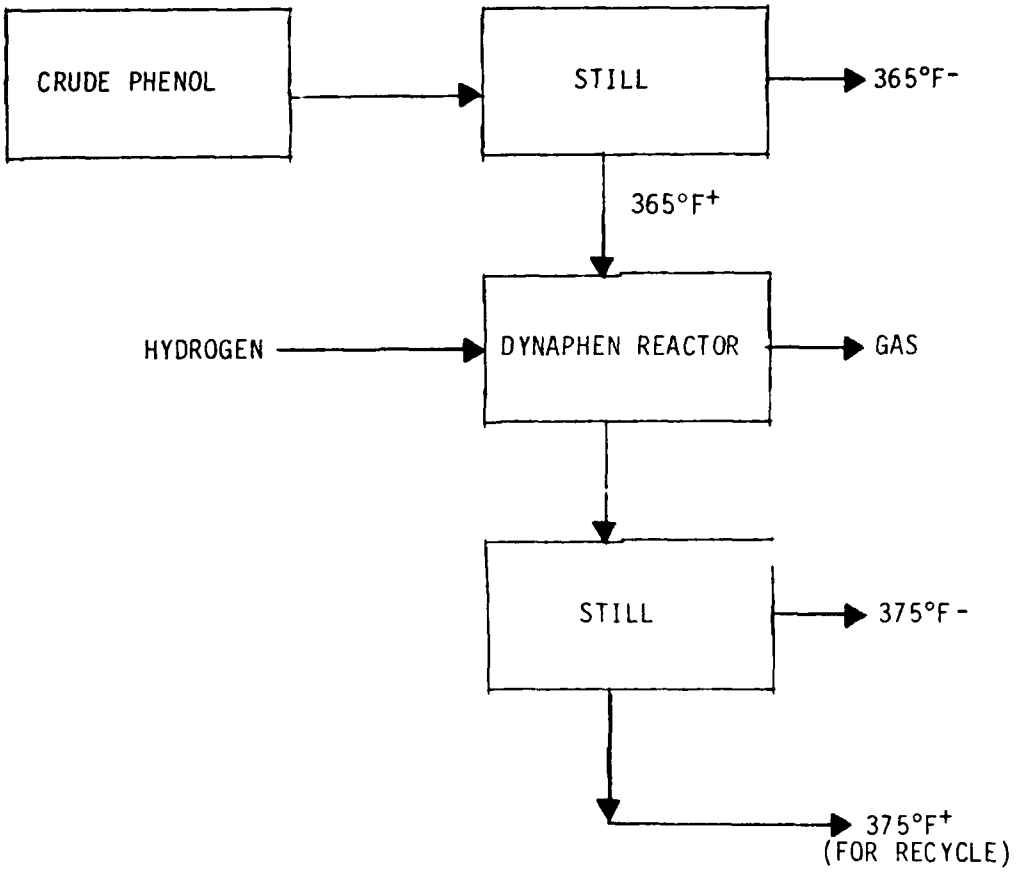
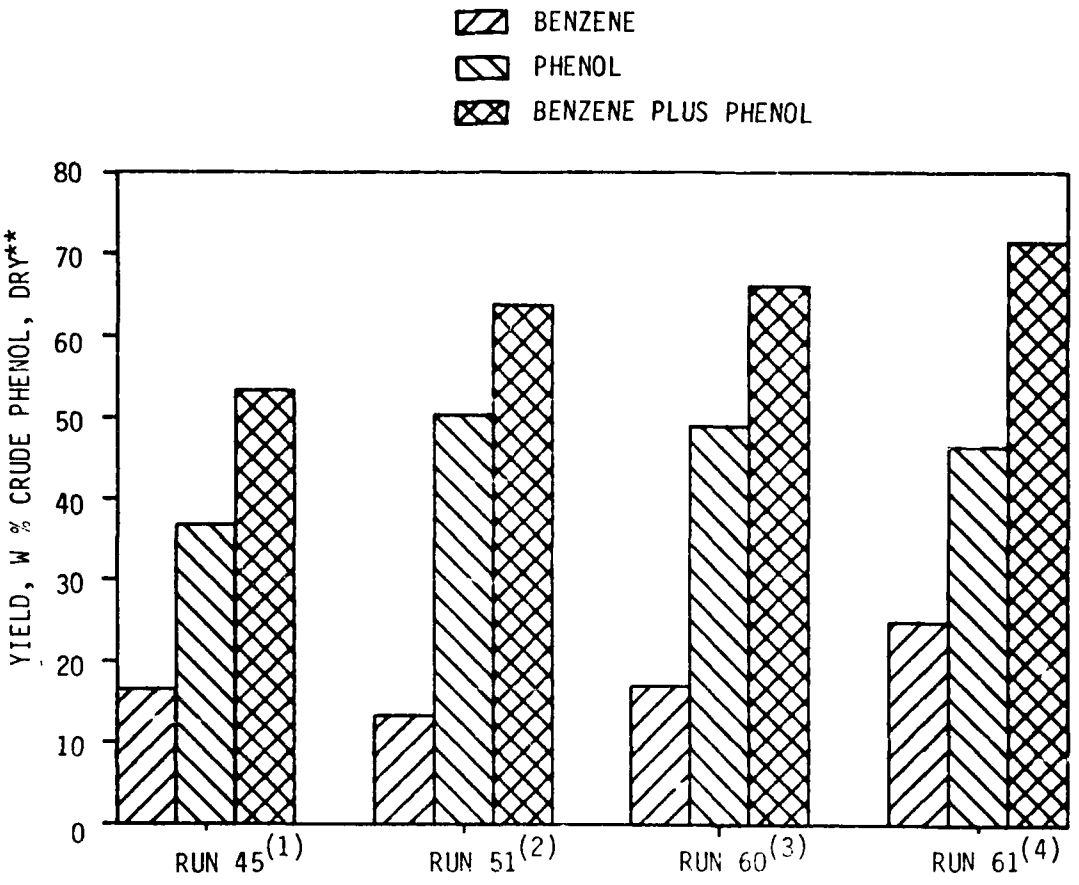


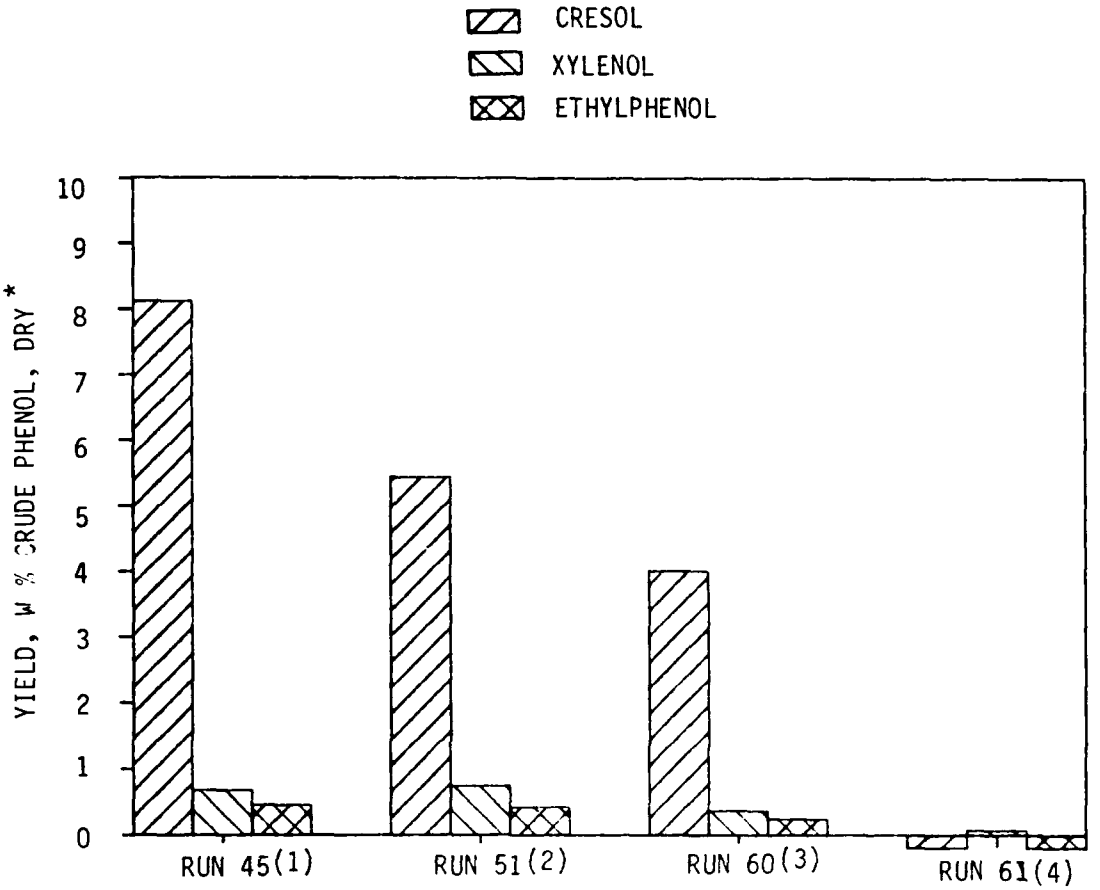
FIGURE 21. CONTINUOUS ONCE-THROUGH TEST



*Phenol yields include the phenol in the 365 F⁻ cut.
**Whole Crude Phenol Content:
45.9 W % Phenol and 0.1 W % Benzene on a dry basis.

(1) Run 45 was a process variable run with whole crude.
(2) Run 51 was a process variable run with cut crude.
(3) Run 60 was a continuous once-through test.
(4) Run 61 was a demonstration recycle test.
Yields calculated on a recycle basis.

FIGURE 22. 1260°F, 600 PSIG, 30 SECONDS - BENZENE AND PHENOL YIELDS*

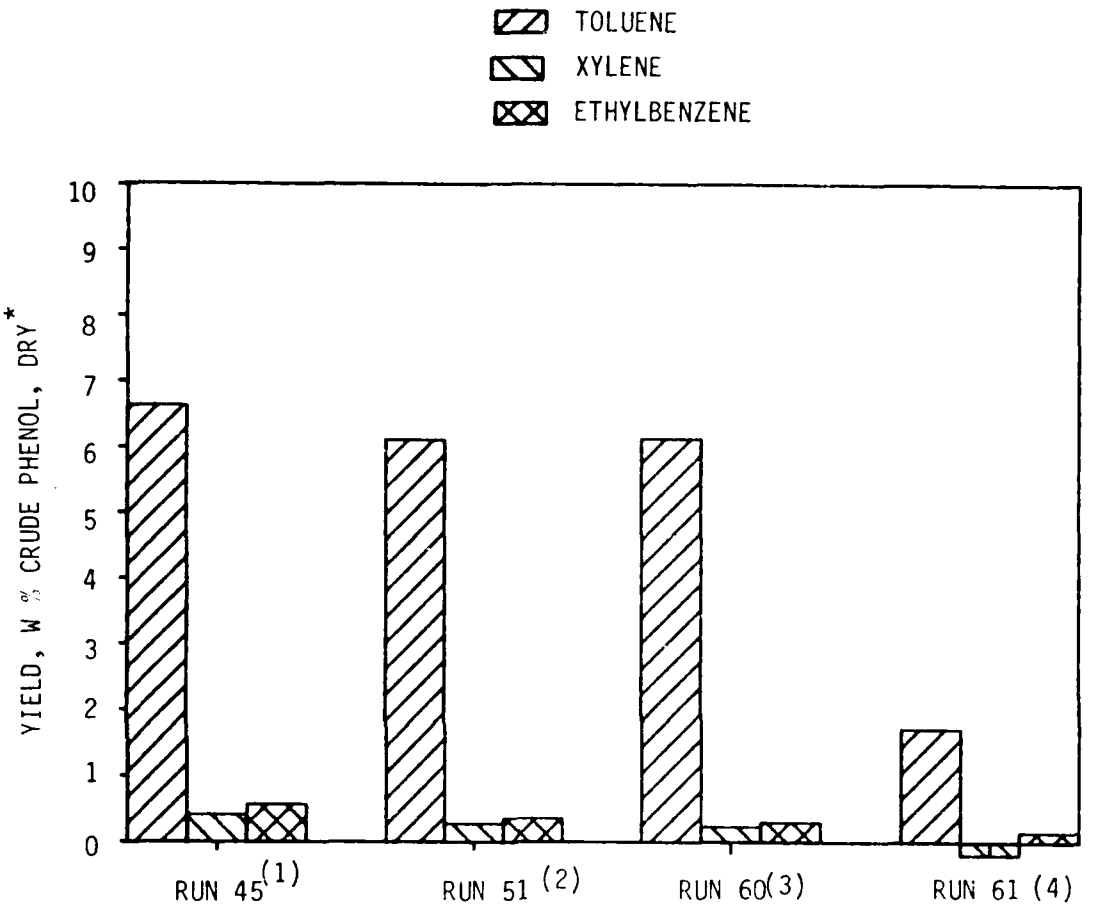


*CRUDE PHENOL CONTENT, DRY BASIS

Cresol	31.9 W %
Xylenol	9.4 W %
Ethylphenol	4.2 W %

(1) Run 45 was a process variable run with whole crude.
(2) Run 51 was a process variable run with cut crude.
(3) Run 60 was a continuous once-through test.
(4) Run 61 was a demonstration recycle test.
Yields calculated on a recycle basis.

FIGURE 23. 1260°F, 600 PSIG, 30 SECONDS - CRESOL, XYLENOL AND ETHYLPHENOL



*CRUDE PHENOL CONTENT, DRY BASIS

Toluene	0.3 W %
Xylene	0.2 W %
Ethylbenzene	0.2 W %

(1) Run 45 was a process variable run with whole crude.
(2) Run 51 was a process variable run with cut crude.
(3) Run 60 was a continuous once-through test.
(4) Run 61 was a demonstration recycle test.
Yields calculated on a recycle basis.

FIGURE 24. 1260°F, 600 PSIG, 30 SECONDS - TOLUENE, XYLENE AND ETHYLBENZENE

TABLE 5. CONTINUOUS ONCE-THROUGH AND DEMONSTRATION RECYCLE RESULTS

Gas Yields and Hydrogen Consumption, W % Dry Reactor Feed

Run	C_1	C_2	C_3	CO	CO_2	Total Gas	Hydrogen Consumption
60	9.0	6.5	1.0	6.2	0.2	23.1	2.7
61-SP*	11.5	9.3	1.1	5.4	1.2	28.7	3.6
61-RCY**	13.7	11.0	1.3	6.5	1.4	34.0	4.2

Liquid Yields, W % Dry Reactor Feed

Run	Benzene	Phenol	Cresol	Xylenol	Ethyl-Phenol	Toluene	Xylene	Ethyl-Benzene
60	24.4	24.5	5.7	0.5	0.4	8.8	0.3	0.4
61-SP*	27.9	17.1	4.1	0.2	0.2	9.6	0.3	0.3
61-RCY**	35.6	21.1	-1.1	0.1	-0.3	2.5	-0.2	0.2

* Run 61-SP refers to calculation yield around the reactor only.

**Run 61-RCY refers to calculation yield around the reactor and the recycle loop.

TASK 4 - DEMONSTRATION RECYCLE TEST

Run 61 was a demonstration recycle operation. The yields and the liquid product from the continuous once-through test (Run 60) were used to calculate the race and composition of the recycled material.

Recycle rate was calculated from a preliminary material balance of the continuous once through test. Gas, water, benzene and phenol yields were subtracted from the total normalized yield to get the recycle to dry cut phenol feed ratio. The resultant ratio was 0.2 to 1.0 recycle to cut phenol ratio. A TBP still was utilized to make a 365°F cut of the continuous once-through test liquid product. The 365°F$^+$ cut of the liquid product was found to contain 55 W % phenol by GC analysis. Further separation was then performed on the 365°F$^+$ cut to produce a 375°F$^+$ cut with only 4.9 W % phenol, as shown in Table D-4. The 375°F$^+$ material was then mixed with toluene, xylene and ethylbenzene to complete the recycle compostion. A commercial plant probably would recycle these alkylbenzenes to increase benzene production.

Toluene, xylene and ethylbenzene concentration in Run 60 dry liquid product was 13.4 W %. Total dry liquid product less benzene and phenol was 31.3 W %. The recycle blend therefore was comprised of 42.9 W % added alkylbenzenes and 57.1 W % 375°F$^+$ material from the continuous once-through test. Refer to Table 1 for the combined analysis of this recycle material.

The liquid material fed to the reactor in the demonstration run was:

Deionized Water	10.0 W %
Cut Phenol	74.9 W %
Recycle Material	15.1 W %

Normalized yields are summarized in Table 5 with additional details in Appendix C. These yields were calculated by two methods. First, as a single-pass operation with the combination of the recycle material, water and the cut phenol being the reactor feed. The second calculation represented a recycle operation with the cut phenol and water being the unit charge. Net liquid product was then calculated by subtracting the recycle stream for the collected liquid. This resulted in negative net yields for xylene, cresol

and ethylphenol. Only the recycle calculation results are discussed in this report.

Benzene, phenol and water yields were 35.6, 21.1 and 19.4 W %, respectively. These components account for 95.4 W % of the liquid yields from the recycle run. Commercially, the net toluene, 2.5% yield, would be recycled to make additional benzene. The cresylics acids, xylenes, ethylbenzenes and heavies in the feed were nearly totally consumed in the recycle run.

Comparing the demonstration test with the continuous once-through test, recycle increased benzene yield by 11.2 W %. Phenol yield decreased 3.4 W %. Cresylic acid and alyklbenzene yields were lower in the recycle operation by 7.9 and 7.4 W %, respectively. Total gas, methane and C_2 gas yields were 10.9, 4.7 and 4.5 W % higher in the recyle operation. Hydrogen comsumption was higher in the recycle operation, 4.2 versus 2.7 W % in Run 60.

These results indicate only a 6.6% increase in phenol yield after recycle, compared to 19.1% in the continuous test and 33.8% in process variable study. It appears, that the conditions chosen for the recycle operation were more severe than those which optimize phenol production.

Figure 25 is a graphic presentation of the recycle operation. The demonstration run liquid yields are presented in Figures 22-24 along the yield from three other runs at similar operating conditions. Whole and cut feed data from the process variable study Runs 45 and 51 are presented along with the results from the continuous once-through test. Where appropriate (Runs 51, 60 and 61), the calculated quantity of phenol in the distillation overhead stream was added to the Dynaphen phenol yield. All yields are presented on a dry crude phenol basis.

The total phenol and benzene yields after distillation and Dynaphen recycle processing were 46.56 W % and 24.93 W % for a total of 71.49 W % total product.

The benzene and phenol yields from two of the process variable study runs, the continuous once through test and the demonstration recycle run have also been compared in Table 6. Using a basis of 900 barrel per day of crude phenol production, commercial Dynaphen yields were projected for each of these four operations. This calculation is a projection of phenol and benzene yields and should not be used as a basis for process guarantees or product

recoveries. Three of these operations produced phenol yields in excess of 400 barrels/day while the recycle mode produced an additional 259 barrels of benzene. The total volumetric yield from the recycle operation corresponds to over 660 barrels/day or 73.4 V % of the as-made crude phenol stream.

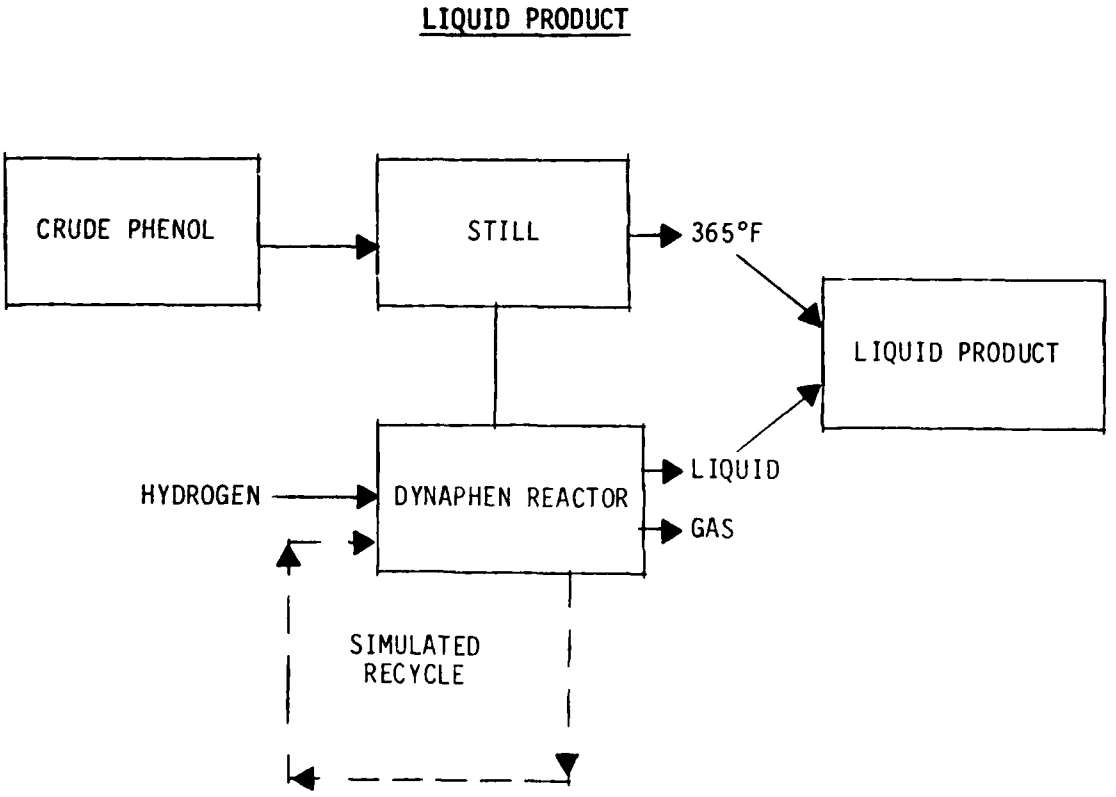


FIGURE 25. DEMONSTRATION TEST WITH RECYCLE

TABLE 6. PROJECTED COMMERCIAL DYNAPHEN YIELDS

Basis: GPGP Crude Phenol Rate - 900 Bbl/Day

DYNAPHEN OPERATION	YIELDS, BBLS/DAY PHENOL	BENZENE	TOTAL
Whole Feed - Single Pass (Run 45)	317	173	490
Cut Phenol - Single Pass Plus Distillation (Run 51)	435	139	574
Cut Phenol - Single Pass Plus Distillation (Run 60)	423	178	601
Cut Phenol - Recycle Operation Plus Distillation (Run 61)	402	259	661

SPECIAL ANALYSES

Quality Assurance/Quality Control Program

HRI conducted a quality assurance and quality control program with regard to the liquid GC analysis performed during this project. Known quantities of pure components were blended together. Routinely, one of these test blends was analyzed with each set of liquid product samples. These QA/QC analysis are presented in Appendix E.

Selected Samples

A total of eight samples were sent to the University of North Dakota Energy and Mineral Research Center (UNDEMRC) and to GPGP for GC analysis. These samples were:

Whole Feed Process Variable Study	-	Run 45 Liquid Product Run 46 Liquid Product As-received Crude Phenol
Cut Feed Process Variable Study	-	Run 50 Liquid Product Run 51 Liquid Product Cut Phenol
Demonstration Recycle Test	-	Run 61 Liquid Product Run 61 Recycle Material

These results are summarized in Tables 7 through 10.

GPGP Results - GPGP used an internal standard in their GC analysis of six of these eight samples. The Run 51 liquid product and the Run 61 recycle material samples were not analyzed by GPGP. Only values for benzene, toluene, phenol, o-cresol, m,p-cresol and water were reported by GPGP.

GPGP analytical results indicate the Dynaphen Process increased the product value even more than was indicated by HRI's analysis. This is because:

- GPGP reported a lower phenol content in the whole crude and the cut crude phenols.
- GPGP reported a higher phenol content in the Run 61 liquid product.
- The differences in the phenol analysis more than offset the lower benzene concentrations reported by GPGP.

UNDEMRC Results - There are differences between HRI and UNDEMRC results, including:

- UNDEMRC reported higher phenol concentration than HRI for all of the samples except the recycled material.
- UNDEMRC reported lower benzene values than HRI reported for the Runs 45, 46, 51 and 61 samples.
- UNDEMRC generally reported higher benzene plus phenol contents than HRI.

Again the outside laboratory analytical results indicate the Dynaphen Process increased the product value even more than was indicated by HRI's analysis.

These differences may be due to:

1. Analytical Variability
2. Different Instrumentation
3. Differences in Quantitative Techniques

A chromatogram of a millivolt signal versus retention time is produced during a GC analysis. The area of each peak is then weighted by response factors. A weight percent for each component is then calculated by:

Multiplicative-Type Response Factors

$$W\ \%\ \text{of component } i = \frac{\text{peak}(i) \times \text{response factor}(i)}{\text{sum of all } (\text{peak}(i) \times \text{response factor}(i))}$$

or

Divisional-Type Response Factors

$$W\ \%\ \text{of component } i = \frac{\text{peak}(i)/\text{response factor}(i)}{\text{sum of all } (\text{peak}(i)/\text{response factor}(i))}$$

HRI developed multiplicative-type response factors using pure components and referenced each response factor to phenol. UNDEMRC used divisional-type response factors, mostly textbook values. For comparison purposes, the response factors used by UNDEMRC were converted to multiplicative-type factors and referenced to phenol. Table 11 presents HRI's response factors and the modified UNDEMRC response factors. The differences in these factors may have contributed significantly to the different results, keeping in mind that GC response factors vary with concentration level, type of detector and type of column.

Additional information concerning the UNDEMRC data is available in Appendix F.

Heteroatom Analysis

Each of these samples was analyzed for nitrogen and sulfur content by HRI analytical personnel. These results are presented in Appendix D. Nitrogen content in these liquid products ranged from 0.43 W % to 0.59 W % of the as-recovered product. Sulfur content was 0.02 W % or less in each of these products. The heteroatom inspection of the Run 60's 375°F$^+$ material indicated 73 W % of the unaccounted for nitrogen and 25% of unaccounted for sulfur were in the 375°F$^+$ portion of the liquid product.

TABLE 7. SPECIAL SAMPLE GC ANALYSIS

Whole and Cut Phenol Feeds

Sample	HRI-5511			L-731		
Description	As-Received Phenol			Cut Phenol		
Laboratory	HRI	UNDEMRC	ANG	HRI	UNDEMRC	ANG
Benzene, W % dry	0.1	0.0	0.0	0.0	0.0	0.0
Toluene	0.3	0.2	0.0	0.0	0.0	0.1
Xylenes	0.2	0.2		0.1	0.0	
Ethylbenzene	0.2	0.1		0.2	0.0	
Phenol	45.9	47.1	33.9	19.8	25.4	16.5
o-Cresol	8.8	7.7	6.3	8.0	7.9	6.0
m,p-Cresol	23.1	19.3	18.0	32.8	29.1	25.6
Ethylphenols	4.2	0.0		5.7	0.0	
Xylenols	9.4	6.7		16.1	8.9	
Catechol	0.9	1.7		3.1	2.7	
Resorcinol	0.0	0.0		0.3	0.0	
Guaiacol	2.6	1.8		3.4	2.6	
Pyridine	0.0	0.0		0.1	0.0	
Lights(1)	0.7	0.1		0.1	0.3	
Heavies(2)	3.6	15.1		10.3	23.1	
Total	100.0	100.0	58.2	100.0	100.0	48.2
Benzene Plus Phenol	46.0	47.1	33.9	19.8	25.4	16.5

(1)This corresponds to aniline in the UNDEMRC analysis.

(2)UNDEMRC heavies content was calculated be subtracting the total of the compounds identified above from 100.

TABLE 8. SPECIAL SAMPLE GC ANALYSIS

Liquid Products From Whole Crude Runs 45 and 46

Sample	Run 45			Run 46		
Laboratory	HRI	UNDEMRC	ANG	HRI	UNDEMRC	ANG
Benzene, W % dry	22.8	13.2	17.6	54.3	39.7	42.0
Toluene	9.1	5.8	7.8	6.1	5.0	7.7
Xylenes	0.6	0.7		0.1	0.1	
Ethylbenzene	0.8	0.4		0.3	0.1	
Phenol	50.4	63.2	49.7	30.4	44.6	33.9
o-Cresol	2.1	1.5	1.4	0.2	0.2	0.1
m,p-Cresol	9.0	9.2	9.0	1.6	1.5	1.3
Ethylphenols	0.6	0.0		0.0	0.0	
Xylenols	0.9	0.8		0.4	0.0	
Catechol	0.0	0.0		0.0	0.0	
Resorcinol	0.0	0.0		0.0	0.0	
Guaiacol	0.5	0.0		0.2	0.0	
Pyridine	0.6	0.0		1.6	0.0	
Lights(1)	0.0	0.0		0.0	0.2	
Heavies(2)	2.6	5.2		4.8	8.6	
Total	100.0	100.0	85.5	100.0	100.0	85.0
Benzene plus Phenol	73.2	76.4	67.3	84.7	84.3	75.9

(1)This corresponds to aniline in the UNDEMRC analysis.

(2)UNDEMRC heavies content was calculated be subtracting the total of the compounds identified above from 100.

TABLE 9. SPECIAL SAMPLES GC ANALYSIS

Liquid Products From Wet Cut Phenol Runs 50 and 51

Sample	Run 50			Run 51	
Laboratory	HRI	UNDEMRC	ANG	HRI	UNDEMRC
Benzene, W % dry	8.4	8.4	7.2	26.9	19.5
Toluene	9.4	8.7	9.0	12.3	9.7
Xylenes	1.0	1.6		0.6	0.8
Ethylbenzene	1.2	1.0		0.7	0.6
Phenol	38.5	46.0	38.3	37.4	50.1
o-Cresol	5.4	4.2	4.5	1.6	1.1
m,p-Cresol	23.5	19.7	22.7	9.4	9.0
Ethylphenols	2.5	0.0		0.9	0.0
Xylenols	3.7	3.1		1.5	0.4
Catechol	0.0	0.4		0.0	0.0
Resorcinol	0.4	0.0		0.2	0.0
Guaiacol	1.1	0.0		0.6	0.0
Pyridine	0.3	0.0		1.2	0.0
Lights(1)	0.3	0.4		0.0	0.0
Heavies(2)	4.3	6.5		6.7	8.8
Total	100.0	100.0	81.7	100.0	100.0
Benzene Plus Phenol	46.9	54.4	45.5	64.3	69.6

(1)This corresponds to aniline in the UNDEMRC analysis.

(2)UNDEMRC heavies content was calculated be subtracting the total of the compounds identified above from 100.

TABLE 10. SPECIAL SAMPLES GC ANALYSIS

Liquid Samples From Demonstration Run

Sample	Liquid Product			Recycled Material	
Laboratory	HRI	UNDEMRC	ANG	HRI	UNDEMRC
Benzene, W % dry	42.1	34.6	36.9	0.0	0.0
Toluene	14.4	12.8	13.8	39.8	39.3
Xylenes	0.4	0.5		2.0	2.4
Ethylbenzene	0.5	0.4		1.6	1.7
Phenol	25.8	35.8	31.6	2.8	2.1
o-Cresol	0.8	0.4	0.3	0.8	0.4
m,p-Cresol	5.4	5.0	5.9	25.1	14.3
Ethylphenols	0.3	0.0		2.0	0.0
Xylenols	0.2	0.3		0.6	1.2
Catechol	0.0	0.0		0.7	0.1
Resorcinol	0.2	0.0		1.0	0.0
Guaiacol	0.4	0.0		0.0	0.0
Pyridine	1.6	0.0		0.2	0.0
Lights(1)	0.2	0.3		0.0	0.2
Heavies(2)	7.7	9.9		23.4	38.3
Total	100.0	100.0	88.5	100.0	100.0
Benzene and Phenol	67.9	70.4	68.5	2.8	2.1

(1)This corresponds to aniline in the UNDEMRC analysis.

(2)UNDEMRC heavies content was calculated be subtracting the total of the compounds identified above from 100.

TABLE 11. RESPONSE FACTORS

LABORATORY	HRI[1]	UNDEMRC[2,3] (MODIFIED)
Benzene	0.79	0.50
Toluene	0.93	0.52
Xylenes	0.93	0.55
Ethylbenzene	0.91	0.55
Phenol	1.00	1.00
o-Cresol	1.18	0.81
m-Cresol	1.23	0.81
p-Cresol	1.15	0.81
2-Ethylphenol	1.02	0.75
3-Ethylphenol	1.11	0.75
4-Ethylphenol	1.08	0.75
2,3 & 3,5 Xylenol	1.05	0.75
2,4 & 2,5 Xylenol	1.16	0.75
2,6 Xylenol	1.10	0.75
3,4 Xylenol	1.06	0.75
Catechol	1.76	1.12
Resorcinol	1.65	1.12
Guaiacol	1.42	0.98
Pyridine	1.42	-

(1) Refer to Appendix B for a description of the GC Column, detector and instruments used by HRI.

(2) Refer to Appendix F for a description of the GC Column, detector and instruments used by UNDEMRC.

(3) These modified UNDEMRC response factors were calculated by inverting the UNDEMRC response factors shown in Appendix F and then referencing them to the original UNDEMRC phenol response factor, i.e.:

$$\text{Modified Response Factor(i)} = \frac{1/\text{original response factor(i)}}{1/\text{original phenol response factor}}$$

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The feasibility of converting GPGP crude phenols to phenol and benzene via Dynaphen Process has been demonstrated.

The net selectivity of the reaction in the Dynaphen reactor is to benzene rather phenol when the reactor feed has a high phenol content as in the case of the as-received crude phenol (45.9 W %, dry).

Positive net phenol yields were demonstrated by processing the cut phenol feedstock which had less than 20 W % phenol content.

A preferred operating region of 600 psig, 30 seconds residence time and reaction temperatures between 1180 and 1260°F was identified for GPGP feedstocks. At 1220°F, the phenolic content of a cut feed was increased by more 50%.

Near-extinction-recycle operation within this preferred region of operation was demonstrated. Benzene, phenol and water accounted for more than 95 W % of the demonstration run liquid product.

RECOMMENDATIONS

Dynaphen product separation requirements are not simple and need to be evaluated. Water is known to azeotrope with benzene, toluene and xylene. Other azeotropes may exist in this system. Additionally, there are at least twelve compounds which boil between 395°F and 441°F in this system. The ability to produce commercial grades of phenol and benzene from Dynaphen products needs to be demonstrated.

The incentive for Dynaphen Processing of various phenolic feedstocks needs to evaluated. These feeds include:

- whole crude phenols
- phenol extracted cresylics
- naphtha plus phenols or cresylics

Dynaphen operation with each of these streams has merit. Whole crude phenol operation should produce significant quantities of benzene, some phenol and be easier to process/separate than the whole crude. Cresylic operation should increase phenol yields and produce significant quantities of benzene. Naphtha operation should produce benzene. The economics of each of these GPGP options needs to be evaluated.

Experimental work on any selected feedstock should be conducted to optimize the production of phenol and benzene.

A kinetic model to predict phenol and benzene yields should be developed.

Engineering design and economic evaluations should be conducted. A Dynaphen unit can then be constructed and operated, if this evaluation is positive.

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APPENDIX A

DYNAPHEN^{sm} CHEMISTRY

DYNAPHEN^{sm} CHEMISTRY

Table A-1 presents the basic Dynaphen^{sm} compounds.

There are several reactions occurring simultaneously in the Dynaphen^{sm} Process. The most important reactions can be summarized as shown in Table A-2. Each of these reactions is thought to be a reversible reaction. However, in the temperature range of interest the equilibrium constant of each of these reactions is thought to be very high, above 1,000. As a result, these reactions are essentially irreversible at reactor conditions.

Maximum benzene and phenol yields for the feeds which were examined in this program are presented Table A-3.

This summary groups each of the isomers of the same compound together, reducing the number of reactions from 30 to 10. In a detailed kinetic discussion this would not be correct, but for potential yield calculations it is adequate.

TABLE A-1. TYPICAL DYNAPHEN COMPOUNDS

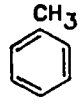
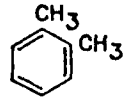
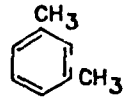
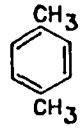
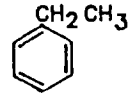
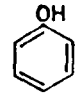
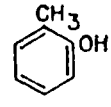
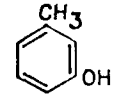
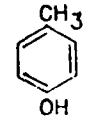
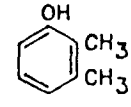
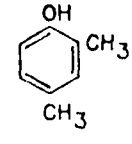
COMPOUND	STRUCTURE	FORMULA	MOLECULAR WEIGHT	BOILING POINT °K	MELTING POINT °K
BENZENE		C_6H_6	78.1134	353.24	278.7
TOLUENE		C_7H_8	92.1412	383.78	178.1
O-XYLENE		C_8H_{10}	106.167	409.50	248.0
M-XYLENE		C_8H_{10}	106.167	412.27	225.3
P-XYLENE		C_8H_{10}	106.167	411.52	286.4
ETHYLBENZENE		C_8H_{10}	106.167	409.34	178.2
PHENOL		C_6H_6O	94.1126	455.02	314.1
O-CRESOL		C_7H_8O	108.1396	464.19	304.1
M-CRESOL		C_7H_8O	108.1396	475.42	285.4
P-CRESOL		C_7H_8O	108.1396	475.13	307.9
2,3-XYLENOL		$C_8H_{10}O$	122.1664	490.07	348.2
2,4-XYLENOL		$C_8H_{10}O$	122.1664	484.13	297.7

TABLE A-1. TYPICAL DYNAPHEN COMPOUNDS (Concluded)

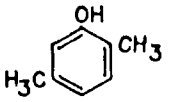
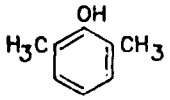
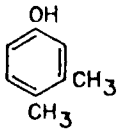
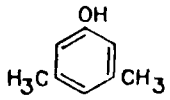
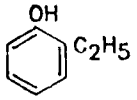
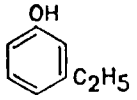
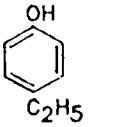
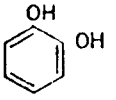
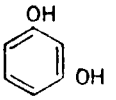
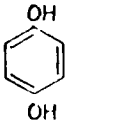
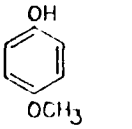
COMPOUND	STRUCTURE	FORMULA	MOLECULAR WEIGHT	BOILING POINT °K	MELTING POINT °K
2,5-XYLENOL		$C_8H_{10}O$	122.1664	484.33	348.0
2,6-XYLENOL		$C_8H_{10}O$	122.1664	474.10	322.0
3,4-XYLENOL		$C_8H_{10}O$	122.1664	500.15	338.3
3,5-XYLENOL		$C_8H_{10}O$	122.1664	494.39	336.4
O-ETHYLPHENOL		$C_8H_{10}O$	122.1664	477.67	269.8
M-ETHYLPHENOL		$C_8H_{10}O$	122.1664	491.57	269.2
P-ETHYLPHENOL		$C_8H_{10}O$	122.1664	491.00	318.0
CATECHOL		$C_6H_6O_2$	110.1122	518.70	377.0
RESORCINOL		$C_6H_6O_2$	110.1122	549.00	383.2
HYDROQUINONE		$C_6H_6O_2$	110.1122	558.00	443.0
GUAIACOL		$C_7H_8O_2$	124.1390	478.20	301.7
PYRIDINE		C_5H_5N	79.1012	388.31	231.0

TABLE A-2. BASIC DYNAPHEN REACTIONS

Basic Reaction	Number of Isomeric Reactions
1. xylenol + hydrogen => cresol + methane	6
2. xylenol + hydrogen => xylene + water	6
3. ethylphenol + hydrogen => phenol + methane	3
4. ethylphenol + hydrogen => ethylbenzene + methane	3
5. cresol + hydrogen => phenol + methane	3
6. cresol + hydrogen => toluene + methane	3
7. phenol + hydrogen => benzene + methane	1
8. ethylbenzene + hydrogen => benzene + ethane	1
9. xylene + hydrogen => toluene + methane	3
10. toluene + hydrogen => benzene + methane	1
Total number of reactions	30

TABLE A-3. POTENTIAL CRUDE PHENOL YIELD CALCULATION, W % FF DRY

Compound	Amount in Crude Phenol	Maximum Benzene Yield	Maximum Phenol Yield
Xylenol	9.4	6.0	7.2
Ethylphenol	4.2	2.7	3.2
Cresol	31.9	23.0	27.8
Phenol	45.9	38.1	45.9
Xylene	0.2	0.1	0.0
Ethylbenzene	0.2	0.1	0.0
Toluene	0.3	0.3	0.0
Total	92.1	70.3	84.1

POTENTIAL CUT PHENOL YIELD CALCULATION, W % FF DRY

Compound	Amount in Cut Phenol	Maximum Benzene Yield	Maximum Phenol Yield
Xylenol	16.1	10.3	12.4
Ethylphenol	5.7	3.6	4.4
Cresol	40.8	29.5	27.8
Phenol	19.8	16.4	19.8
Xylene	0.1	0.1	0.0
Ethylbenzene	0.2	0.1	0.0
Toluene	0.0	0.0	0.0
Total	82.8	60.0	64.4
Total, W % Dry Crude Phenol		42.0	45.1
Distillation plus Dynaphen Total W % Dry Crude Phenol		42.0	77.0

APPENDIX B

MAJOR EQUIPMENT DESCRIPTIONS

MAJOR EQUIPMENT DESCRIPTIONS

DYNAPHEN^{sm} UNIT DESCRIPTION

The process testing bench scale unit utilized for Dynaphen^{sm} operations is also used for Hydrodealkylation (HDA) Process. It is comprised of an isothermal HDA reactor followed by liquid/vapor separation vessels. Figure B-1 is a schematic flowsheet of the unit.

The reactor consists of a continuous length of 9/16 inch x 3/16 inch stainless steel 347 tubing, about 18 feet long and cold-formed into a coil of 5 inch I.D. and 12 inch length. The reactor is maintained at isothermal conditions by immersing the reactor coil in a fluidized bed of fine alumina particles that are heated by four 750 Watt "calrod" heaters placed along the inside perimeter of the fluidized bed. The alumina particles are fluidized by an air stream passing through a porous plate distributor at the bottom of the chamber. An air-powered suction type dust collector draws off the fine particles that become airborne from around the top of the fluidized bed enclosure. Almost instantaneous heat transfer is achieved between the reactor fluid and the fluidized bed, since the heat transfer coefficients across the reactor tubing are of the order of 60-120 BTU/Hr/Ft^2°F (for the fluidized bed) and 40-60 BTU/Hr/Ft^2°F (for the reactor fluid). Higher heat transfer rates are further facilitated by using a narrow reactor with a very high L/D ratio.

The liquid feed to the unit is supplied from a 2-1/2 inch glass vessel with a capacity of 1000cc. The glass vessel is mounted on a digital weigh-scale providing on-line feed supply rate (gm/hr) information. The liquid is metered into the system using a small vertical check pump with a maximum capacity of about 480cc per hour. Hydrogen feed to the unit is drawn from plant supply at 2800 psig and reduced by a regulator to 1500 psig for the unit supply pressure. Hydrogen flow is regulated by a control valve downstream of the orifice and it joins the liquid feed before the feed preheater.

The feed preheater consists of 69 inches of stainless steel 347 tubing (9/16 inch x 5/16 inch) wrapped with 832 Watt resistance tape. Two thermocouples are located at 38 inches and 8 inches before the reactor inlet elbows, and both measure the external skin temperatures. The preheater is insulated with Kaowool insulation.

Liquid and gas products from the reactor are collected and cooled in a high pressure receiver followed by a low pressure receiver where the remaining gas/liquid separation is completed. The high pressure receiver is about 80 inches long and is tempered water-jacketed to condense all the liquid products. Product liquid flows continuously to the low pressure receiver under level control. The low pressure receiver is a 2 inch stainless steel pipe, 24 inch long with a total volume of about 1160cc, and the upper half is water-jacketed. Liquid products are accumulated over the entire run period in the LP receiver and are drawn-off at the end of the run. The vent gases leaving the high and low pressure receiver are passed through 2 cold traps and a knockout vessel piped in series to remove any remaining condensible vapors like benzene. The gas is sampled and then metered in a wet test meter before finally discharged to the flare system.

GAS CHROMATOGRAPHS

Liquid products from the runs were analyzed with a Perkin Elmer Model Sigma 3 gas chromatograph and a Sigma 10B Data console. The GC was equipped with a single flame ionization detector and one 5 foot x 1/8 inch O.D. x 1.8mm glass column packed with 0.5% SP-100 (an ester of Carbowax 20M and terephthalic acid) on 80/100 mesh Carbopak C (graphite). The column is available from Supelco, Inc., Bellefonte, Pennsylvania. Injector and detector temperatures were maintained at 250°C and 300°C, respectively. The column temperature was programmed from 150°C (after a 2 minute hold) at 8°C/minute to 225°C (followed by a 30 minutes hold). The sample size was 0.3 microliter and helium was the carrier gas at 20cc/minute. Component identification was through retention time correlation. Calibration standards were at the same general concentration levels found in the product samples. A 24-component matrix and internal normalization to the phenol peak were used in the quantification by weight percent. All samples were homogenized in an equal weight of isopropanal prior to GC (and Karl Fischer moisture) analyses.

The gas samples were analyzed with a Hewlett-Packard Model 5880A refinery gas analyzer/GC equipped with four standard columns used in an RGA.

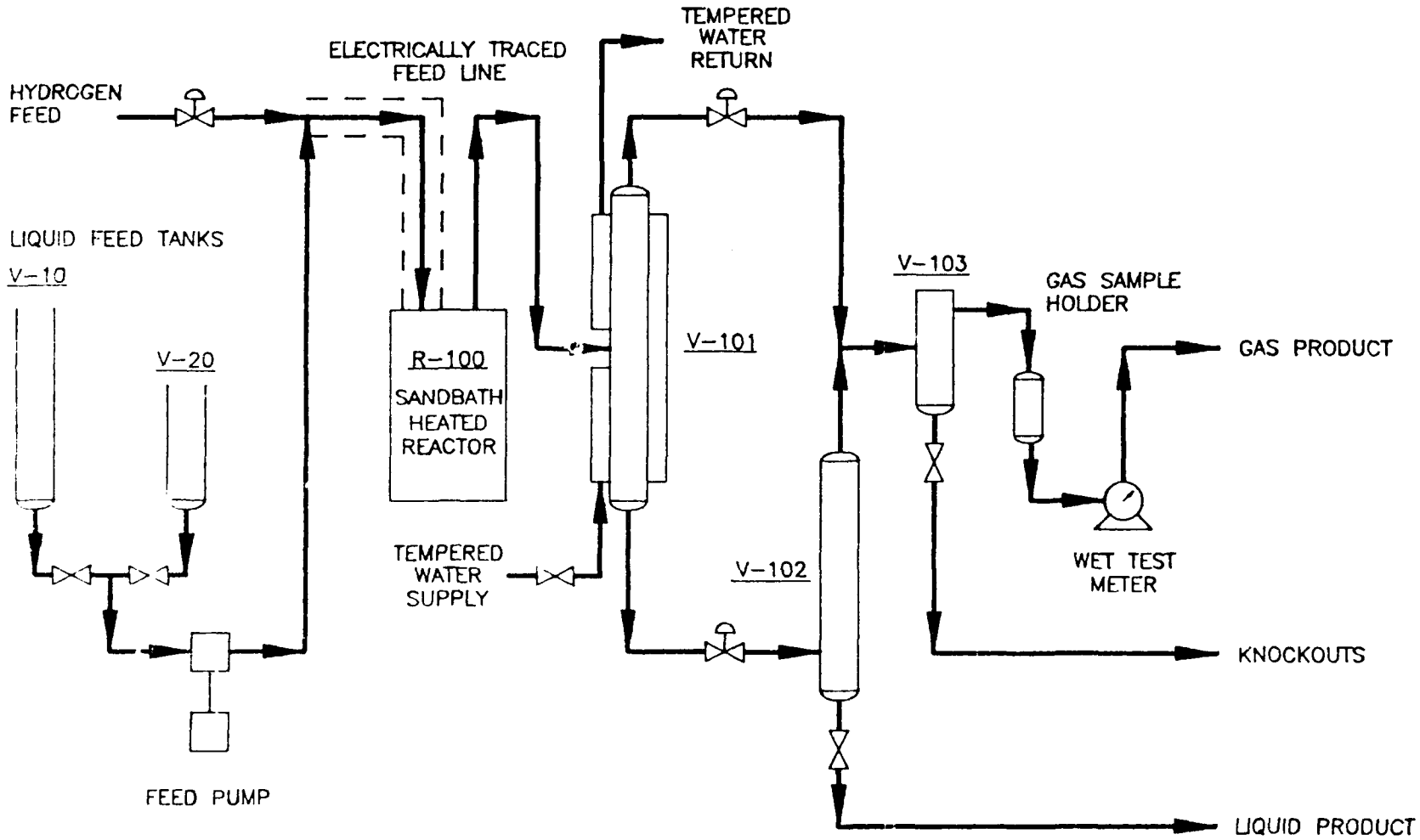


FIGURE B-1. PROCESS FLOW DIAGRAM OF THE UNIT

APPENDIX C

SUMMARY OF NORMALIZED YIELDS

TABLE C-1. PROCESS VARIABLE STUDY - SUMMARY OF NORMALIZED YIELDS

WHOLE CRUDE PHENOL RUNS

RUN	42	43	44	45	46
PRESSURE, PSIG	< ----------		600		---------- >
RESIDENCE TIME, SECONDS	29.2	29.0	28.8	28.7	28.5
REACTOR TEMPERATURE, °F	1100	1150	1200	1250	1300
GAS YIELDS, W % FEED					
C1	1.48	3.38	6.66	9.70	12.50
C_2s	1.08	2.13	3.79	5.50	6.95
C_3s	0.91	1.82	2.30	1.32	0.64
C_4s	0.72	1.20	0.42	0.00	0.00
CO	2.53	3.94	6.36	7.00	7.14
CO_2	0.10	0.26	0.23	0.34	0.38
H_2S	0.02	0.02	0.00	0 00	0.00
Other	0.39	0.14	0.06	0.00	0.00
TOTAL	7.23	12.89	19.82	23.86	27.61
LIQUID YIELDS, W % FEED					
Benzene	1.14	2.25	6.04	15.79	34.14
Toluene	1.54	2.64	4.59	6.31	3.82
Xylenes	0.34	0.50	0.57	0.40	0.07
Ethylbenzenes	0.44	0.79	0.92	0.55	0.17
Phenol	41.14	40.73	39.06	35.01	19.14
Cresols	27.77	24.33	17.39	7.72	1.17
Xylenols	6.21	4.17	2.10	0.65	0.23
Ethylphenols	3.74	3.02	1.72	0.44	0.03
Guaiacol	0.84	0.65	0.66	0.36	0.10
Pyridine	0.03	0.05	0.00	0.39	1.05
Water	5.02	5.62	6.34	8.77	12.58
Lights	0.08	0.00	0.00	0.00	0.00
Heavies	4.41	2.87	2.01	1.80	3.01
Nitrogen(1)	0.47	0.47	0.48	0.41	0.29
Sulfur(1)	0.05	0.06	0.07	0.07	0.07
TOTAL	93.22	88.15	81.95	78.67	75.87
HYDROGEN CONSUMPTION, W % FEED	0.45	1.04	1.77	2.53	3.45
AROMATIC ANALYSIS					
% Alpha C Removed	10.2	21.6	39.9	64.0	87.2
% Alpha OH Removed	9.7	19.0	32.0	49.0	71.7
% Rings Preserved	94.0	89.2	84.1	82.4	80.5

(1)Liquid nitrogen and sulfur contents were calculated by material balance. These quantities should be added to the reported heavies content to get the total heavies make.

TABLE C-2. PROCESS VARIABLE STUDY - SUMMARY OF NORMALIZED YIELDS

DRY CUT CRUDE PHENOL RUNS

RUN	47	48	49
PRESSURE, PSIG	< ---------- 600 ---------- >		
RESIDENCE TIME, SECONDS	29.9	29.7	29.6
REACTOR TEMPERATURE, °F	1140	1180	1220
GAS YIELDS, W % FEED			
C1	4.33	6.24	7.04
C_2s	2.83	4.64	5.13
C_3s	2.15	2.41	2.01
C_4s	1.80	0.72	0.42
CO	7.53	7.08	7.02
CO_2	0.20	0.41	0.28
H_2S	0.04	0.04	0.04
Other	0.36	0.04	0.04
TOTAL	19.23	21.58	21.98
LIQUID YIELDS, W % FEED			
Benzene	1.26	4.04	8.01
Toluene	3.24	6.20	8.33
Xylenes	0.47	0.86	0.83
Ethylbenzenes	0.57	0.95	0.88
Phenol	22.36	26.30	29.90
Cresols	34.14	26.60	20.05
Xylenols	7.40	4.07	2.09
Ethylphenols	4.68	2.76	1.39
Guaiacol	1.16	1.02	0.89
Pyridine	0.11	0.19	0.30
Water	0.24	2.04	3.58
Lights	0.12	0.15	0.21
Heavies	5.61	4.48	3.05
Nitrogen(1)	0.53	0.52	0.50
Sulfur(1)	0.04	0.04	0.04
TOTAL	81.93	80.22	80.05
HYDROGEN CONSUMPTION, W % FEED	1.16	1.80	2.03
AROMATIC ANALYSIS			
% Alpha C Removed	23.54	37.66	49.66
% Alpha OH Removed	27.35	36.15	43.47
% Rings Preserved	84.62	83.97	85.19

(1)Liquid nitrogen and sulfur contents were calculated by material balance. These quantities should be added to the reported heavies content to get the total heavies make.

TABLE C-3. PROCESS VARIABLE STUDY - SUMMARY OF NORMALIZED YIELDS

WET CUT CRUDE PHENOL RUNS

RUN	50	51	52	53	54
PRESSURE, PSIG	< ----- 600 ----- >			900	600
RESIDENCE TIME, SECONDS	27.8	27.7	27.6	29.7	46.3
REACTOR TEMPERATURE, °F	1220	1260	1300	1260	1260
GAS YIELDS, W % FEED					
C1	5.92	8.96	9.99	9.09	10.15
C_2s	4.40	6.24	7.15	6.34	6.18
C_3s	1.93	1.14	0.29	1.17	0.21
C_4s	0.46	0.13	0.05	0.14	0.03
CO	6.32	6.59	6.38	6.69	5.68
CO_2	0.26	0.34	0.25	0.34	0.34
H_2S	0.05	0.03	0.01	0.03	0.00
Other	0.00	0.00	0.00	0.00	0.00
TOTAL	19.34	23.43	24.12	23.80	22.59
LIQUID YIELDS, W % FEED					
Benzene	5.98	17.57	38.75	25.73	37.91
Toluene	6.71	8.04	3.48	6.83	4.08
Xylenes	0.69	0.38	0.05	0.20	0.06
Ethylbenzenes	0.86	0.48	0.10	0.28	0.12
Phenol	27.39	24.37	11.90	21.04	13.73
Cresols	20.59	7.15	0.83	3.80	1.04
Xylenols	2.65	0.98	0.39	0.55	0.31
Ethylphenols	1.76	0.56	0.29	0.29	0.16
Guaiacol	0.80	0.40	0.15	0.23	0.09
Pyridine	0.24	0.78	1.39	1.12	1.50
Water	10.68	13.47	17.56	15.13	17.72
Lights	0.18	0.00	0.00	0.00	0.00
Heavies	3.33	4.50	3.74	3.33	3.38
Nitrogen(1)	0.47	0.37	0.26	0.31	0.24
Sulfur(1)	0.02	0.04	0.05	0.04	0.07
TOTAL	82.35	79.09	78.94	78.88	80.41
HYDROGEN CONSUMPTION, W % FEED	1.69	2.52	3.06	2.68	3.00
AROMATIC ANALYSIS					
% Alpha C Removed	45.73	70.58	91.10	79.85	90.10
% Alpha OH Removed	38.68	55.67	78.09	65.60	76.77
% Rings Preserved	85.68	84.37	86.25	85.33	87.82

(1)Liquid nitrogen and sulfur contents were calculated by material balance. These quantities should be added to the reported heavies content to get the total heavies make.

TABLE C-4. CONTINUOUS AND RECYCLE STUDIES - SUMMARY OF NORMALIZED YIELDS

CUT CRUDE PHENOL RUNS

RUN	60	61-SP(1)	61-RCY(2)
PRESSURE, PSIG	< ----------	600	---------- >
RESIDENCE TIME, SECONDS	27.3	27.7	27.7
REACTOR TEMPERATURE, °F	< ----------	1260	---------- >
GAS YIELDS, W % FEED			
C1	8.10	10.36	12.19
C_2s	5.85	8.37	9.85
C_3s	0.88	1.02	1.20
C_4s	0.09	0.05	0.06
CO	5.59	4.90	5.78
CO_2	0.21	1.06	1.25
H_2S	0.03	0.03	0.04
Other	0.00	0.00	0.00
TOTAL	20.75	25.79	30.37
LIQUID YIELDS, W % FEED			
Benzene	21.93	25.15	31.80
Toluene	7.89	8.63	2.19
Xylenes	0.31	0.23	-0.15
Ethylbenzenes	0.41	0.29	0.02
Phenol	22.09	15.39	18.85
Cresols	5.16	3.68	-1.01
Xylenols	0.48	0.14	+0.05
Ethylphenols	0.20	0.18	-0.21
Guaiacol	0.32	0.27	0.34
Pyridine	1.09	0.93	1.15
Water	17.29	17.08	19.40
Lights	0.18	0.14	0.17
Heavies	4.01	4.74	0.48
Nitrogen(3)	0.30	0.52	0.29
Sulfur(3)	0.04	0.04	0.04
TOTAL	81.70	77.41	73.41
HYDROGEN CONSUMPTION, W % FEED	2.45	3.20	3.78
AROMATIC ANALYSIS			
% Alpha C Removed	75.15	77.83	98.23
% Alpha OH Removed	61.56	67.96	78.55
% Rings Preserved	87.18	81.50	78.46

(1)Run 61 (single-pass) results are obtained by doing the material balance around the reactor only.

(2)Run 61 (recycle) results are obtained by doing the material balance around the reactor and the liquid recycle.

(3)Liquid nitrogen and sulfur contents were calculated by material balance. These quantities should be added to the reported heavies content to get the total heavies make.

APPENDIX D

LIQUID PRODUCT ANALYSIS

TABLE D-1. PROCESS VARIABLE STUDY - LIQUID PRODUCT ANALYSIS

WHOLE CRUDE PHENOL RUNS

RUN	42	43	44	45	46
PRESSURE, PSIG	< ----------		600		---------- >
RESIDENCE TIME, SECONDS	29.2	29.0	28.8	28.7	28.5
REACTOR TEMPERATURE, °F	1100	1150	1200	1250	1300
HETEROATOM ANALYSIS, W %					
Nitrogen	-	-	-	0.47	0.43
Sulfur	-	-	-	0.01	0.01
Karl Fischer, W % Water	6.9	8.0	9.7	13.8	20.4
GC ANALYSIS - DRY BASIS, W %					
Benzene	1.3	2.7	8.0	22.8	54.3
Toluene	1.8	3.2	6.1	9.1	6.1
M-Xylene	0.4	0.6	0.8	0.6	0.1
Ethylbenzene	0.5	1.0	1.2	0.8	0.3
Phenol	46.9	49.7	52.0	50.4	30.4
o-Cresol	8.6	7.9	5.5	2.1	0.2
m-Cresol	14.1	13.5	11.3	6.3	1.3
p-Cresol	9.0	8.3	6.3	2.7	0.3
2-Ethylphenol(1)	0.9	0.8	0.5	0.1	0.0
3-Ethylphenol	1.7	1.5	1.1	0.4	0.0
4-Ethylphenol	1.7	1.3	0.7	0.1	0.0
2,3 & 3,5 Xylenol	2.3	1.7	1.0	0.3	0.0
2,4 & 2,5 Xylenol	2.7	2.1	1.0	0.2	0.1
2,6 Xylenol	0.5	0.4	0.3	0.1	0.0
3,4 Xylenol	1.5	0.9	0.6	0.3	0.3
Catechol	1.2	0.0	0.0	0.0	0.0
Resorcinol	0.3	0.4	0.3	0.0	0.0
Guaiacol	1.0	0.8	0.9	0.5	0.2
Pyridine	0.0	0.1	0.0	0.6	1.6
Lights	0.1	0.0	0.0	0.0	0.0
Heavies	3.5	3.1	2.4	2.6	4.8
TOTAL	100.0	100.0	100.0	100.0	100.0

(1)Includes Hydroquinone.

TABLE D-2. PROCESS VARIABLE STUDY - LIQUID PRODUCT ANALYSIS

DRY CUT CRUDE PHENOL RUNS

RUN	47	48	49
PRESSURE, PSIG	< ----------	600	---------- >
RESIDENCE TIME, SECONDS	29.9	29.7	29.6
REACTOR TEMPERATURE, °F	1140	1180	1220
HETEROATOM ANALYSIS, W %			
Nitrogen	--	--	--
Sulfur	--	--	--
Karl Fischer, W % Water	2.6	3.9	5.1
GC ANALYSIS - DRY BASIS, W %			
Benzene	1.6	5.2	10.6
Toluene	4.0	8.0	11.0
M-Xylene	0.6	1.1	1.1
Ethylbenzene	0.7	1.2	1.2
Phenol	27.6	33.9	39.4
o-Cresol	9.0	7.1	5.0
m-Cresol	20.2	17.3	14.1
p-Cresol	12.9	9.9	7.3
2-Ethylphenol(1)	1.1	0.7	0.4
3-Ethylphenol	2.4	1.7	1.1
4-Ethylphenol	2.3	1.1	0.3
2,3 & 3,5 Xylenol	3.0	2.0	1.1
2,4 & 2,5 Xylenol	3.8	1.9	0.9
2,6 Xylenol	0.8	0.5	0.2
3,4 Xylenol	1.5	0.9	0.5
Catechol	0.0	0.0	0.0
Resorcinol	0.7	0.6	0.4
Guaiacol	1.4	1.3	1.2
Pyridine	0.1	0.2	0.4
Lights	0.1	0.2	0.3
Heavies	6.2	5.2	3.5
TOTAL	100.0	100.0	100.0

(1)Includes Hydroquinone

TABLE D-3. PROCESS VARIABLE STUDY - LIQUID PRODUCT ANALYSIS

WET CUT CRUDE PHENOL RUNS

RUN	50	51	52	53	54
PRESSURE, PSIG	< ----- 600 ----- >			900	600
RESIDENCE TIME, SECONDS	27.8	27.7	27.6	29.7	46.3
REACTOR TEMPERATURE, °F	1220	1260	1300	1260	1260
HETEROATOM ANALYSIS, W %					
Nitrogen	0.46	0.59	--	--	--
Sulfur	0.02	0.02	--	--	--
Karl Fischer, W % Water	19.5	23.3	30.8	23.7	25.7
GC ANALYSIS - DRY BASIS, W %					
Benzene	8.4	26.9	63.5	40.5	60.8
Toluene	9.4	12.3	5.7	10.8	6.5
M-Xylene	1.0	0.6	0.1	0.3	0.1
Ethylbenzene	1.2	0.7	0.2	0.4	0.2
Phenol	38.5	37.4	19.5	33.2	22.0
o-Cresol	5.4	1.6	0.2	0.7	0.2
m-Cresol	15.2	6.8	0.9	4.0	1.2
p-Cresol	8.3	2.6	0.2	1.3	0.3
2-Ethylphenol(1)	0.5	0.1	0.1	0.1	0.0
3-Ethylphenol	1.4	0.4	0.1	0.2	0.1
4-Ethylphenol	0.6	0.4	0.3	0.2	0.2
2,3 & 3,5 Xylenol	1.4	0.4	0.0	0.2	0.1
2,4 & 2,5 Xylenol	1.2	0.5	0.2	0.2	0.0
2,6 Xylenol	0.3	0.1	0.0	0.1	0.0
3,4 Xylenol	0.8	0.5	0.4	0.4	0.4
Catechol	0.0	0.0	0.0	0.0	0.0
Resorcinol	0.4	0.2	0.0	0.0	0.0
Guaiacol	1.1	0.6	0.2	0.4	0.1
Pyridine	0.3	1.2	2.3	1.8	2.4
Lights	0.3	0.0	0.0	0.0	0.0
Heavies	4.3	6.7	6.1	5.2	5.4
TOTAL	100.0	100.0	100.0	100.0	100.0

(1)Includes Hydroquinone

TABLE D-4. CONTINUOUS AND RECYCLE STUDIES - LIQUID PRODUCT ANALYSIS

CUT CRUDE PHENOL RUNS

RUN	60	61-SP(1)	61-RCY(2)
PRESSURE, PSIG	< ---------- 600 ---------- >		
RESIDENCE TIME, SECONDS	27.3	27.7	27.7
REACTOR TEMPERATURE, °F	< ---------- 1260 ---------- >		
HETEROATOM ANALYSIS, W %			
Nitrogen	0.58	0.49	2.60
Sulfur	0.02	0.02	0.100
Karl Fischer, W % Water	23.7	20.8	0.00
GC ANALYSIS - DRY BASIS, W %			
Benzene	34.2	42.1	0.0
Toluene	12.3	14.4	0.8
M-Xylene	0.5	0.4	0.0
Ethylbenzene	0.6	0.5	0.0
Phenol	34.5	25.8	4.9
o-Cresol	1.1	0.8	1.3
m-Cresol	5.2	3.9	34.4
p-Cresol	1.8	1.5	9.7
2-Ethylphenol(2)	0.1	0.1	0.4
3-Ethylphenol	0.2	0.2	2.1
4-Ethylphenol	0.0	0.0	1.0
2,3 & 3,5 Xylenol	0.2	0.0	0.0
2,4 & 2,5 Xylenol	0.0	0.0	1.0
2,6 Xylenol	0.1	0.2	0.0
3,4 Xylenol	0.4	0.0	0.0
Catechol	0.0	0.0	0.6
Resorcinol	0.1	0.2	1.9
Guaiacol	0.5	0.4	0.0
Pyridine	1.7	1.6	0.3
Lights	0.3	0.2	0.0
Heavies	6.2	7.7	41.6
TOTAL	100.0	100.0	100.0

(1) The 375°F+ cut was 10.3 W % of Run 60 liquid product.
(2) Includes Hydroquinone

APPENDIX E

QUALITY ASSURANCE/QUALITY CONTROL ANALYSES

TABLE E-1. QUALITY ASSURANCE/QUALITY CONTROL ANALYSES

	ACTUAL AMOUNT IN BLEND	MEASUREMENTS		
BLEND NO. 1, PREPARED 12/8/87				
Compound, W %		12/29/87	1/22/88	1/29/88
Phenol	41.2	41.2	41.7	42.0
o-Cresol	6.6	6.6	6.5	6.7
m-Cresol	7.2	7.2	7.2	7.2
p-Cresol	6.5	6.6	6.6	6.6
2,4 Xylenol	26.9	27.0	26.8	26.1
3-Ethylphenol	8.7	8.6	8.5	8.5
Guaiacol	1.8	1.8	1.7	1.9
Pyridine	1.1	1.0	1.0	1.0
Total	100.0	100.0	100.0	100.0
BLEND NO. P-2, PREPARED 12/8/87				
Compound, W %			12/10/87	
o-Cresol	80.0		79.9	
2-Ethylphenol	1.1		1.1	
3-Ethylphenol	1.7		1.8	
4-Ethylphenol	5.4		5.4	
2,6 Xylenol	1.0		1.0	
2,4 Xylenol	3.2		3.2	
2,3 & 3,5 Xylenol	3.7		3.7	
3,4 Xylenol	3.9		3.9	
Total	100.0		100.0	
BLEND NO. 8, PREPARED 12/10/87				
Compound, W %		12/28/87		1/6/88
Benzene	25.7	24.8		24.0
Toluene	13.3	13.8		13.8
Ethylbenzene	11.8	11.7		11.8
Xylene	36.7	38.4		38.9
2,6 Xylenol	5.3	5.1		5.2
Phenol	7.2	6.2		6.3
Total	100.0	100.0		100.0
BLEND NO. 13, PREPARED 12/19/87				
Compound, W %			12/29/87	
Phenol	34.8		34.2	
Benzene	9.6		8.9	
Toluene	2.7		2.6	
Ethylbenzene	3.3		3.1	
m-Xylene	2.9		2.8	
Pyridine	1.0		1.1	
2,4 Xylenol	45.7		47.3	
Total	100.0		100.0	
BLEND NO. 20A, PREPARED 1/15/88				
Compound, W %		1/25/88		1/29/88
Benzene	27.3	25.3		24.1
Toluene	54.2	57.4		58.6
Ethylbenzene	3.2	2.8		3.0
m-Xylene	3.3	3.1		3.2
Phenol	8.2	7.0		7.2
2-Ethylphenol	1.3	1.5		1.2
3-Ethylphenol	1.3	1.5		1.4
4-Ethylphenol	1.2	1.4		1.3
Total	100.0	100.0		100.0

APPENDIX F

UNDEMRC LIQUID PRODUCT ANALYSES

HRI SAMPLES ANALYSES

This appendix was taken in part from Dr. Curtis Knudsen's letter to Everette C. Harris, March 14, 1988.

Table F-1 presents the data for the samples as they were received and analyzed at UNDEMRC in comparison to values obtained by HRI. In general, the data is in fair agreement. Of the five samples containing isopropanol, two are essentially the same while the others are plus or minus about 10%.

The total peaks present in the GC output are indicated in Table F-1 as well as the number of peaks that are over 0.1 A% (A% = Area %). The sum of the total peaks is 100 A%, while the sum of the peaks of over 0.1 A% was usually greater than 97%, indicating that the small peaks do not contain much material. The difference in the number of peaks is related to the amount of the sample that was injected to the GC. In addition, some samples contain less of certain compounds. Compounds in low concentrations may not be observed. In Tables F-2 through F-11, a period indicates a peak was not observed.

GC equipment used and conditions were as follows:

GC: HP Model 5890
MS: HP Model 5985B

Column: DB-5, fused silica, 5% phenyl-methylsilicon bonded phase, film thickness 0.25 micron, 0.25mm I.D., 6m long.

Injected: 0.02 microliters, neat

Conditions: 0°C for 2 minutes followed by 6°C/minute to 320°C.

Table F-2 presents a summary of the data for the HRI-5511, 237-61RC, and L-731 samples. The KF-water values were determined by Karl Fischer analyses and calculated into the GC data to obtain as-received analyses values. The latter two samples contained larger quantities of heavier material that does not show up on this

printout. If requested, a more complete printout can be obtained. Calculations were performed using 100*Kwt%/Uwt% = amount left where Kwt% is the value for a compound in the HRI-5511 sample and Uwt% is the value in the L-731 sample. These calculations indicate that the L-731 sample represents 63 W % of the HRI-5511 sample in which the heavier material has been concentrated.

Table F-3 presents a summary of the data, on an isopropanol-free basis, for the samples that initially contained isopropanol. The raw GC data for the samples (including response factors) is given in Tables F-4 through F-11 for comparison with your data.

TABLE F-1. ANALYSES OF AS-RECEIVED DYNAPHEN SAMPLES[a]

Sample ID	Isopropanol, wt% HRI[c]	Isopropanol, wt% EMRC	# GC Peaks Total	# GC Peaks over 0.1 A%	Total[b] A%
HRI5511	0.00	0.00	124	59	96.9
237-45	35.55	31.84	46	23	98.7
237-46	41.51	42.22	44	17	98.6
237-50	33.57	37.29	104	31	97.6
237-51	47.23	44.91	32	27	99.6
237-61	50.03	49.72	80	21	98.5
237-61RC	0.00	0.00	147	53	95.7
L-731	0.00	0.00	168	63	95.7

(a) All values are for the as-received (AR) samples. Samples with a positive isopropanol value were received with the isopropanol present. HRI values were obtained from letters sent with the samples or verbally.

(b) This is the total A% (A% = Area%) in the peaks which were over 0.1 A%.

(c) HRI added isopropanol to the liquid product samples to produce a homogeneous single phase liquid for analysis. Without the isopropanol, several liquid products were two-phase. HRI's values were calculated from blending data.

TABLE F-2. GC/MS SUMMARY DATA, ISOPROPANOL-FREE IN WT%

#	Compound / Sample	HR15511	237-61RC	L-731
1.	KF-Water	5.45	0.17	0.09
2.	Isopropanol	.	.	.
3.	Benzene	.	0.03	.
4.	Toluene	0.16	39.22	.
5.	C2-Benzene	0.08	1.69	.
6.	mp-Xylene	0.12	2.22	.
7.	o-Xylene	0.07	0.14	0.01
8.	Aniline	0.13	0.21	0.28
9.	Phenol	44.55	2.14	25.38
10.	C3-Benzene	0.04	.	0.05
11.	Indane	0.02	.	.
12.	Indene	0.05	.	.
13.	o-Cresol	7.30	0.41	7.87
14.	mp-Cresol	18.22	14.25	29.11
15.	Guaiacol	1.65	.	2.63
16.	C2-Phenol	0.30	.	0.44
17.	C2-Phenols	1.34	0.13	0.01
18.	C2-Phenol	0.98	.	2.42
19.	C2-Phenol	1.38	1.10	2.24
20.	C2-Phenol	2.36	.	3.82
21.	Naphthalene	0.26	7.22	0.38
22.	C1-Guaiacol	0.08	0.22	0.13
23.	Catechol	1.59	0.10	2.66
24.	C3-Phenol	0.16	0.01	0.20
25.	C3-Phenol	0.18	.	0.29
26.	Quinoline	0.03	1.49	0.07
27.	C1-Catechol	1.76	0.07	2.76
28.	C3-Phenol	0.17	0.19	0.19
29.	C3-Phenol	0.16	.	0.18
30.	2-Methylnaphthalene	0.22	1.43	0.20
31.	1-Methylnaphthalene	0.24	0.45	0.39
32.	C2-Catechol	0.87	0.03	1.35
33.	Biphenyl	0.05	2.21	0.07
34.	C2-Catechol	0.91	0.02	1.62
35.	Acenaphthene	0.03	0.94	0.05
36.	Dibenzofuran	0.06	1.25	0.10
37.	Naphthol	0.41	1.46	0.61
38.	Phenanthrene	0.08	2.75	0.11
39.	Fluoranthene	0.02	0.69	0.02
40.	Pyrene	0.02	0.53	0.03
	Total wt%	91.51	82.77	85.73
	# of GC Peaks	38	30	33

KF-Water = Karl Fischer water.

TABLE F-3. GC/MS SUMMARY DATA, ISOPROPANOL-FREE IN WT%

#	Compound / Sample	237-45	237-46	237-50	237-51	237-61
1.	KF-Water	13.61	20.89	22.36	24.47	21.15
2.	Isopropanol	.	.	.	.	.
3.	Benzene	11.43	31.39	6.49	14.76	27.26
4.	Toluene	4.98	3.97	6.74	7.31	10.06
5.	C2-Benzene	0.36	0.09	0.78	0.42	0.28
6.	mp-Xylene	0.52	0.09	1.02	0.53	0.32
7.	o-Xylene	0.08	.	0.22	0.08	0.05
8.	Aniline	.	0.15	0.27	.	0.27
9.	Phenol	54.61	35.29	35.73	37.87	28.21
10.	C3-Benzene	.	.	0.01	.	.
11.	Indane	0.17	0.08	0.29	0.22	0.14
12.	Indene	0.12	0.07	0.16	0.14	0.09
13.	o-Cresol	1.31	0.13	3.24	0.86	0.34
14.	mp-Cresol	7.91	1.15	15.27	6.76	3.90
15.	Guaiacol	.	.	.	.	.
16.	C2-Phenol	.	.	0.10	.	.
17.	C2-Phenols	0.07	.	0.31	.	0.01
18.	C2-Phenol	0.11	.	0.38	.	0.04
19.	C2-Phenol	.	.	0.30	.	0.16
20.	C2-Phenol	0.50	.	1.34	0.29	.
21.	Naphthalene	1.54	2.95	1.26	2.64	3.82
22.	C1-Guaiacol	.	0.05	0.03	.	0.08
23.	Catechol	.	.	0.29	.	.
24.	C3-Phenol	.	.	0.03	.	.
25.	C3-Phenol	.	0.12	0.01	.	0.22
26.	Quinoline	.	.	0.04	.	.
27.	C1-Catechol	.	.	0.14	.	0.06
28.	C3-Phenol	.	.	.	.	.
29.	C3-Phenol	.	.	0.01	.	.
30.	2-Methylnaphthalene	0.19	0.18	0.17	0.23	0.34
31.	1-Methylnaphthalene	0.11	0.04	0.15	0.12	0.07
32.	C2-Catechol	.	.	0.02	.	.
33.	Biphenyl	0.22	0.83	0.12	0.30	0.52
34.	C2-Catechol	.	.	0.06	.	0.01
35.	Acenaphthene	0.13	0.12	0.10	0.20	0.13
36.	Dibenzofuran	0.33	0.53	0.18	0.45	0.41
37.	Naphthol	0.26	0.08	0.36	0.39	0.19
38.	Phenanthrene	0.26	0.49	0.16	0.60	0.57
39.	Fluoranthene	0.07	0.14	0.04	0.18	0.10
40.	Pyrene	0.06	0.10	0.03	0.15	0.07
	Total wt%	98.93	98.96	98.23	98.97	98.85
	# of GC Peaks	24	23	37	99	99

KF-Water = Karl Fischer water.

TABLE F-4. GC/MS ANALYIS DATA FOR MHRI5511

#	Compound	Rf	RT(min)	A%	wt%	AR,wt%
1.	KF-Water	.	.	.	.	5.45
2.	Isopropanol	0.53	2.030	.	.	.
3.	Benzene	1.12	5.142	.	.	.
4.	Toluene	1.07	8.441	0.27	0.17	0.16
5.	C2-Benzene	1.02	11.596	0.12	0.08	0.08
6.	mp-Xylene	1.02	11.847	0.19	0.13	0.12
7.	o-Xylene	1.02	12.590	0.12	0.08	0.07
8.	Aniline	0.75	15.486	0.15	0.13	0.13
9.	Phenol	0.56	15.784	39.85	47.12	44.55
10.	C3-Benzene	1.00	16.573	0.06	0.04	0.04
11.	Indane	1.00	16.940	0.04	0.03	0.02
12.	Indene	1.00	17.206	0.08	0.06	0.05
13.	o-Cresol	0.69	17.710	8.05	7.73	7.30
14.	mp-Cresol	0.69	18.355	20.08	19.27	18.22
15.	Guaiacol	0.57	18.607	1.50	1.75	1.65
16.	C2-Phenol	0.75	19.056	0.36	0.32	0.30
17.	C2-Phenols	0.75	20.201	1.60	1.41	1.34
18.	C2-Phenol	0.75	20.238	1.18	1.04	0.98
19.	C2-Phenol	0.75	20.697	1.65	1.45	1.38
20.	C2-Phenol	0.75	20.777	2.83	2.50	2.36
21.	Naphthalene	0.90	21.049	0.38	0.28	0.26
22.	C1-Guaiacol	0.60	21.185	0.08	0.09	0.08
23.	Catechol	0.50	21.547	1.27	1.69	1.59
24.	C3-Phenol	0.86	22.343	0.22	0.17	0.16
25.	C3-Phenol	0.86	22.507	0.25	0.19	0.18
26.	Quinoline	0.56	22.595	0.02	0.03	0.03
27.	C1-Catechol	0.63	23.105	1.77	1.86	1.76
28.	C3-Phenol	0.86	23.226	0.23	0.18	0.17
29.	C3-Phenol	0.86	23.340	0.22	0.17	0.16
30.	2-Methylnaphthalene	1.00	23.919	0.35	0.23	0.22
31.	1-Methylnaphthalene	1.00	24.288	0.39	0.25	0.24
32.	C2-Catechol	0.76	25.305	1.05	0.92	0.87
33.	Biphenyl	0.92	25.903	0.07	0.05	0.05
34.	C2-Catechol	0.76	26.028	1.11	0.97	0.91
35.	Acenaphthene	0.90	28.285	0.05	0.04	0.03
36.	Dibenzofuran	0.90	28.969	0.09	0.07	0.06
37.	Naphthol	0.85	29.036	0.55	0.43	0.41
38.	Phenanthrene	0.94	34.300	0.13	0.09	0.08
39.	Fluoranthene	0.93	39.285	0.02	0.02	0.02
40.	Pyrene	0.93	40.159	0.03	0.02	0.02
	Total A%, wt%, wt%			86.44	91.02	91.51
	# of Peaks, wt counts			37	151.04	

KF-Water = Karl Fischer water; Rf = FID relative response factor; Rt = GC retention time (min); A% = GC area percent; wt% = weight percent; AR = as received; wt counts = sum of A%/Rf;

TABLE F-5. GC/MS ANALYSIS DATA FOR M237-45

#	Compound	Rf	Rt(min)	A%	wt%	AR,wt%
1.	KF-Water	.	.	.	.	9.23
2.	Isopropanol	0.53	2.030	28.88	35.08	31.84
3.	Benzene	1.12	5.142	14.86	8.54	7.75
4.	Toluene	1.07	8.441	6.18	3.72	3.38
5.	C2-Benzene	1.02	11.596	0.42	0.27	0.24
6.	mp-Xylene	1.02	11.847	0.62	0.39	0.35
7.	o-Xylene	1.02	12.590	0.09	0.06	0.05
8.	Aniline	0.75	15.486	.	.	.
9.	Phenol	0.56	15.784	35.48	40.79	37.03
10.	C3-Benzene	1.00	16.573	.	.	.
11.	Indane	1.00	16.940	0.20	0.13	0.12
12.	Indene	1.00	17.206	0.14	0.09	0.08
13.	o-Cresol	0.69	17.710	1.05	0.98	0.89
14.	mp-Cresol	0.69	18.355	6.33	5.91	5.36
15.	Guaiacol	0.57	18.607	.	.	.
16.	C2-Phenol	0.75	19.056	.	.	.
17.	C2-Phenols	0.75	20.201	0.06	0.05	0.05
18.	C2-Phenol	0.75	20.238	0.09	0.08	0.07
19.	C2-Phenol	0.75	20.697	.	.	.
20.	C2-Phenol	0.75	20.777	0.43	0.37	0.34
21.	Naphthalene	0.90	21.049	1.61	1.15	1.04
22.	C1-Guaiacol	0.60	21.185	.	.	.
23.	Catechol	0.50	21.547	.	.	.
24.	C3-Phenol	0.86	22.343	.	.	.
25.	C3-Phenol	0.86	22.507	.	.	.
26.	Quinoline	0.56	22.595	.	.	.
27.	C1-Catechol	0.63	23.105	.	.	.
28.	C3-Phenol	0.86	23.226	.	.	.
29.	C3-Phenol	0.86	23.340	.	.	.
30.	2-Methylnaphthalene	1.00	23.919	0.22	0.14	0.13
31.	1-Methylnaphthalene	1.00	24.288	0.12	0.08	0.07
32.	C2-Catechol	0.76	25.305	.	.	.
33.	Biphenyl	0.92	25.903	0.23	0.16	0.15
34.	C2-Catechol	0.76	26.028	.	.	.
35.	Acenaphthene	0.90	28.285	0.13	0.10	0.09
36.	Dibenzofuran	0.90	28.969	0.35	0.25	0.22
37.	Naphthol	0.85	29.036	0.25	0.19	0.17
38.	Phenanthrene	0.94	34.300	0.28	0.19	0.18
39.	Fluoranthene	0.93	39.285	0.07	0.05	0.05
40.	Pyrene	0.93	40.159	0.06	0.04	0.04
	Total A%, wt%, wt%			98.16	98.82	98.93
	# of Peaks, wt counts			24	155.30	

KF-Water = Karl Fischer water; Rf = FID relative response factor; Rt = GC retention time (min); A% = GC area percent; wt% = weight percent; AR = as received; wt counts = sum of A%/Rf;

TABLE F-6. GC/MS ANALYSIS DATA FOR M237-46

#	Compound	Rf	Rt(min)	A%	wt%	AR,wt%
1.	KF-Water	.	.	.	.	11.98
2.	Isopropanol	0.53	2.030	36.65	47.96	42.22
3.	Benzene	1.12	5.142	33.02	20.45	18.00
4.	Toluene	1.07	8.441	3.99	2.59	2.28
5.	C2-Benzene	1.02	11.596	0.09	0.06	0.05
6.	mp-Xylene	1.02	11.847	0.09	0.06	0.05
7.	o-Xylene	1.02	12.590	.	.	.
8.	Aniline	0.75	15.486	0.11	0.10	0.09
9.	Phenol	0.56	15.784	18.56	22.99	20.24
10.	C3-Benzene	1.00	16.573	.	.	.
11.	Indane	1.00	16.940	0.07	0.05	0.04
12.	Indene	1.00	17.206	0.07	0.05	0.04
13.	o-Cresol	0.69	17.710	0.09	0.09	0.08
14.	mp-Cresol	0.69	18.355	0.75	0.75	0.66
15.	Guaiacol	0.57	18.607	.	.	.
16.	C2-Phenol	0.75	19.056	.	.	.
17.	C2-Phenols	0.75	20.201	.	.	.
18.	C2-Phenol	0.75	20.238	.	.	.
19.	C2-Phenol	0.75	20.697	.	.	.
20.	C2-Phenol	0.75	20.777	.	.	.
21.	Naphthalene	0.90	21.049	2.49	1.92	1.69
22.	C1-Guaiacol	0.60	21.185	0.03	0.03	0.03
23.	Catechol	0.50	21.547	.	.	.
24.	C3-Phenol	0.86	22.343	.	.	.
25.	C3-Phenol	0.86	22.507	0.09	0.07	0.07
26.	Quinoline	0.56	22.595	.	.	.
27.	C1-Catechol	0.63	23.105	.	.	.
28.	C3-Phenol	0.86	23.226	.	.	.
29.	C3-Phenol	0.86	23.340	.	.	.
30.	2-Methylnaphthalene	1.00	23.919	0.17	0.12	0.11
31.	1-Methylnaphthalene	1.00	24.288	0.04	0.03	0.02
32.	C2-Catechol	0.76	25.305	.	.	.
33.	Biphenyl	0.92	25.903	0.72	0.54	0.48
34.	C2-Catechol	0.76	26.028	.	.	.
35.	Acenaphthene	0.90	28.285	0.10	0.08	0.07
36.	Dibenzofuran	0.90	28.969	0.45	0.35	0.31
37.	Naphthol	0.85	29.036	0.06	0.05	0.05
38.	Phenanthrene	0.94	34.300	0.43	0.32	0.28
39.	Fluoranthene	0.93	39.285	0.13	0.09	0.08
40.	Pyrene	0.93	40.159	0.09	0.07	0.06
	Total A%, wt%, wt%			98.30	98.82	98.96
	# of Peaks, wt counts			23	144.19	

KF-Water = Karl Fischer water; Rf = FID relative response factor; Rt = GC retention time (min); A% = GC area percent; wt% = weight percent; AR = as received; wt counts = sum of A%/Rf;

TABLE F-7. GC/MS ANALYSIS DATA FOR M237-50

#	Compound	Rf	Rt(min)	A%	wt%	AR,wt%
1.	KF-Water	.	.	.	.	13.87
2.	Isopropanol	0.53	2.030	35.69	43.29	37.29
3.	Benzene	1.12	5.142	8.15	4.68	4.03
4.	Toluene	1.07	8.441	8.08	4.86	4.18
5.	C2-Benzene	1.02	11.596	0.89	0.56	0.48
6.	mp-Xylene	1.02	11.847	1.17	0.74	0.63
7.	o-Xylene	1.02	12.590	0.25	0.16	0.14
8.	Aniline	0.75	15.486	0.23	0.19	0.17
9.	Phenol	0.56	15.784	22.42	25.74	22.17
10.	C3-Benzene	1.00	16.573	0.01	0.01	0.01
11.	Indane	1.00	16.940	0.32	0.21	0.18
12.	Indene	1.00	17.206	0.18	0.11	0.10
13.	o-Cresol	0.69	17.710	2.50	2.33	2.01
14.	mp-Cresol	0.69	18.355	11.81	11.00	9.48
15.	Guaiacol	0.57	18.607	.	.	.
16.	C2-Phenol	0.75	19.056	0.08	0.07	0.06
17.	C2-Phenols	0.75	20.201	0.26	0.23	0.19
18.	C2-Phenol	0.75	20.238	0.32	0.28	0.24
19.	C2-Phenol	0.75	20.697	0.26	0.22	0.19
20.	C2-Phenol	0.75	20.777	1.13	0.97	0.83
21.	Naphthalene	0.90	21.049	1.27	0.91	0.78
22.	C1-Guaiacol	0.60	21.185	0.02	0.02	0.02
23.	Catechol	0.50	21.547	0.16	0.21	0.18
24.	C3-Phenol	0.86	22.343	0.03	0.02	0.02
25.	C3-Phenol	0.86	22.507	0.01	0.01	0.01
26.	Quinoline	0.56	22.595	0.02	0.03	0.02
27.	C1-Catechol	0.63	23.105	0.10	0.10	0.08
28.	C3-Phenol	0.86	23.226	.	.	.
29.	C3-Phenol	0.86	23.340	0.01	0.01	0.01
30.	2-Methylnaphthalene	1.00	23.919	0.19	0.12	0.11
31.	1-Methylnaphthalene	1.00	24.288	0.17	0.11	0.09
32.	C2-Catechol	0.76	25.305	0.02	0.01	0.01
33.	Biphenyl	0.92	25.903	0.12	0.08	0.07
34.	C2-Catechol	0.76	26.028	0.05	0.05	0.04
35.	Acenaphthene	0.90	28.285	0.10	0.07	0.06
36.	Dibenzofuran	0.90	28.969	0.18	0.13	0.11
37.	Naphthol	0.85	29.036	0.35	0.26	0.23
38.	Phenanthrene	0.94	34.300	0.17	0.11	0.10
39.	Fluoranthene	0.93	39.285	0.04	0.03	0.02
40.	Pyrene	0.93	40.159	0.03	0.02	0.02
	Total A%, wt%, wt%			96.81	97.95	98.23
	# of Peaks, wt counts			37	155.56	

KF-Water = Karl Fischer water; Rf = FID relative response factor; Rt = GC retention time (min); A% = GC area percent; wt% = weight percent; AR = as received; wt counts = sum of A%/Rf;

TABLE F-8. GC/MS ANALYSIS DATA FOR M237-51

#	Compound	Rf	Rt(min)	A%	wt%	AR,wt%
1.	KF-Water	.	.	.	.	13.37
2.	Isopropanol	0.53	2.030	42.43	51.84	44.91
3.	Benzene	1.12	5.142	16.09	9.30	8.06
4.	Toluene	1.07	8.441	7.62	4.61	3.99
5.	C2-Benzene	1.02	11.596	0.41	0.26	0.23
6.	mp-Xylene	1.02	11.847	0.52	0.33	0.29
7.	o-Xylene	1.02	12.590	0.08	0.05	0.04
8.	Aniline	0.75	15.486	.	.	.
9.	Phenol	0.56	15.784	20.65	23.88	20.69
10.	C3-Benzene	1.00	16.573	.	.	.
11.	Indane	1.00	16.940	0.22	0.14	0.12
12.	Indene	1.00	17.206	0.14	0.09	0.08
13.	o-Cresol	0.69	17.710	0.58	0.54	0.47
14.	mp-Cresol	0.69	18.355	4.54	4.26	3.69
15.	Guaiacol	0.57	18.607	.	.	.
16.	C2-Phenol	0.75	19.056	.	.	.
17.	C2-Phenols	0.75	20.201	.	.	.
18.	C2-Phenol	0.75	20.238	.	.	.
19.	C2-Phenol	0.75	20.697	.	.	.
20.	C2-Phenol	0.75	20.777	0.21	0.18	0.16
21.	Naphthalene	0.90	21.049	2.31	1.66	1.44
22.	C1-Guaiacol	0.60	21.185	.	.	.
23.	Catechol	0.50	21.547	.	.	.
24.	C3-Phenol	0.86	22.343	.	.	.
25.	C3-Phenol	0.86	22.507	.	.	.
26.	Quinoline	0.56	22.595	.	.	.
27.	C1-Catechol	0.63	23.105	.	.	.
28.	C3-Phenol	0.86	23.226	.	.	.
29.	C3-Phenol	0.86	23.340	.	.	.
30.	2-Methylnaphthalene	1.00	23.919	0.22	0.14	0.12
31.	1-Methylnaphthalene	1.00	24.288	0.12	0.08	0.07
32.	C2-Catechol	0.76	25.305	.	.	.
33.	Biphenyl	0.92	25.903	0.27	0.19	0.16
34.	C2-Catechol	0.76	26.028	.	.	.
35.	Acenaphthene	0.90	28.285	0.17	0.12	0.11
36.	Dibenzofuran	0.90	28.969	0.39	0.28	0.24
37.	Naphthol	0.85	29.036	0.33	0.25	0.22
38.	Phenanthrene	0.94	34.300	0.55	0.38	0.33
39.	Fluoranthene	0.93	39.285	0.16	0.11	0.10
40.	Pyrene	0.93	40.159	0.14	0.09	0.08
	Total A%, wt%, wt%			98.17	98.81	98.97
	# of Peaks, wt counts			22	154.44	

KF-Water = Karl Fischer water; Rf = FID relative response factor; Rt = GC retention time (min); A% = GC area percent; wt% = weight percent; AR = as received; wt counts = sum of A%/Rf;

TABLE F-9. GC/MS ANALYSIS DATA FOR M237-61

#	Compound	Rf	Rt(min)	A%	wt%	AR,wt%
1.	KF-Water	.	.	.	.	10.51
2.	Isopropanol	0.53	2.030	43.27	55.56	49.72
3.	Benzene	1.12	5.142	24.92	15.14	13.55
4.	Toluene	1.07	8.441	8.79	5.59	5.00
5.	C2-Benzene	1.02	11.596	0.23	0.16	0.14
6.	mp-Xylene	1.02	11.847	0.26	0.18	0.16
7.	o-Xylene	1.02	12.590	0.04	0.03	0.02
8.	Aniline	0.75	15.486	0.17	0.15	0.13
9.	Phenol	0.56	15.784	12.89	15.66	14.02
10.	C3-Benzene	1.00	16.573	.	.	.
11.	Indane	1.00	16.940	0.11	0.08	0.07
12.	Indene	1.00	17.206	0.07	0.05	0.04
13.	o-Cresol	0.69	17.710	0.19	0.19	0.17
14.	mp-Cresol	0.69	18.355	2.20	2.17	1.94
15.	Guaiacol	0.57	18.607	.	.	.
16.	C2-Phenol	0.75	19.056	.	.	.
17.	C2-Phenols	0.75	20.201	0.01	0.01	0.01
18.	C2-Phenol	0.75	20.238	0.02	0.02	0.02
19.	C2-Phenol	0.75	20.697	0.10	0.09	0.08
20.	C2-Phenol	0.75	20.777	.	.	.
21.	Naphthalene	0.90	21.049	2.80	2.12	1.90
22.	C1-Guaiacol	0.60	21.185	0.04	0.04	0.04
23.	Catechol	0.50	21.547	.	.	.
24.	C3-Phenol	0.86	22.343	.	.	.
25.	C3-Phenol	0.86	22.507	0.15	0.12	0.11
26.	Quinoline	0.56	22.595	.	.	.
27.	C1-Catechol	0.63	23.105	0.03	0.03	0.03
28.	C3-Phenol	0.86	23.226	.	.	.
29.	C3-Phenol	0.86	23.340	.	.	.
30.	2-Methylnaphthalene	1.00	23.919	0.28	0.19	0.17
31.	1-Methylnaphthalene	1.00	24.288	0.05	0.04	0.03
32.	C2-Catechol	0.76	25.305	.	.	.
33.	Biphenyl	0.92	25.903	0.39	0.29	0.26
34.	C2-Catechol	0.76	26.028	0.01	0.01	0.01
35.	Acenaphthene	0.90	28.285	0.10	0.07	0.06
36.	Dibenzofuran	0.90	28.969	0.30	0.23	0.20
37.	Naphthol	0.85	29.036	0.13	0.11	0.09
38.	Phenanthrene	0.94	34.300	0.44	0.32	0.28
39.	Fluoranthene	0.93	39.285	0.08	0.06	0.05
40.	Pyrene	0.93	40.159	0.05	0.04	0.04
	Total A%, wt%, wt%			98.12	98.72	98.85
	# of Peaks, wt counts			29	146.94	

KF-Water = Karl Fischer water; Rf = FID relative response factor; Rt = GC retention time (min); A% = GC area percent; wt% = weight percent; AR = as received; wt counts = sum of A%/Rf;

TABLE F-10. GC/MS ANALYSIS DATA FOR M237-61RC

#	Compound	Rf	Rt(min)	A%	wt%	AR,wt%
1.	KF-Water	.	.	.	.	0.17
2.	Isopropanol	0.53	2.030	.	.	.
3.	Benzene	1.12	5.142	0.03	0.03	0.03
4.	Toluene	1.07	8.441	44.48	39.29	39.22
5.	C2-Benzene	1.02	11.596	1.83	1.69	1.69
6.	mp-Xylene	1.02	11.847	2.40	2.23	2.22
7.	o-Xylene	1.02	12.590	0.15	0.14	0.14
8.	Aniline	0.75	15.486	0.17	0.21	0.21
9.	Phenol	0.56	15.784	1.27	2.15	2.14
10.	C3-Benzene	1.00	16.573	.	.	.
11.	Indane	1.00	16.940	.	.	.
12.	Indene	1.00	17.206	.	.	.
13.	o-Cresol	0.69	17.710	0.30	0.41	0.41
14.	mp-Cresol	0.69	18.355	10.42	14.28	14.25
15.	Guaiacol	0.57	18.607	.	.	.
16.	C2-Phenol	0.75	19.056	.	.	.
17.	C2-Phenols	0.75	20.201	0.10	0.13	0.13
18.	C2-Phenol	0.75	20.238	.	.	.
19.	C2-Phenol	0.75	20.697	0.88	1.10	1.10
20.	C2-Phenol	0.75	20.777	.	.	.
21.	Naphthalene	0.90	21.049	6.88	7.23	7.22
22.	C1-Guaiacol	0.60	21.185	0.14	0.22	0.22
23.	Catechol	0.50	21.547	0.05	0.10	0.10
24.	C3-Phenol	0.86	22.343	0.01	0.01	0.01
25.	C3-Phenol	0.86	22.507	.	.	.
26.	Quinoline	0.56	22.595	0.89	1.50	1.49
27.	C1-Catechol	0.63	23.105	0.05	0.07	0.07
28.	C3-Phenol	0.86	23.226	0.18	0.19	0.19
29.	C3-Phenol	0.86	23.340	.	.	.
30.	2-Methylnaphthalene	1.00	23.919	1.51	1.43	1.43
31.	1-Methylnaphthalene	1.00	24.288	0.47	0.45	0.45
32.	C2-Catechol	0.76	25.305	0.02	0.03	0.03
33.	Biphenyl	0.92	25.903	2.15	2.21	2.21
34.	C2-Catechol	0.76	26.028	0.02	0.02	0.02
35.	Acenaphthene	0.90	28.285	0.90	0.94	0.94
36.	Dibenzofuran	0.90	28.969	1.19	1.25	1.25
37.	Naphthol	0.85	29.036	1.32	1.46	1.46
38.	Phenanthrene	0.94	34.300	2.74	2.75	2.75
39.	Fluoranthene	0.93	39.285	0.68	0.69	0.69
40.	Pyrene	0.93	40.159	0.52	0.53	0.53
	Total A%, wt%, wt%			81.74	82.74	82.77
	# of Peaks, wt counts			29	105.79	

KF-Water = Karl Fischer water; Rf = FID relative response factor; Rt = GC retention time (min); A% = GC area percent; wt% = weight percent; AR = as received; wt counts = sum of A%/Rf;

TABLE F-11, GC/MS ANALYSIS DATA FOR ML-731

#	Compound	Rf	Rt(min)	A%	wt%	AR,wt%
1.	KF-Water	.	.	.	.	0.09
2.	Isopropanol	0.53	2.030	.	.	.
3.	Benzene	1.12	5.142	.	.	.
4.	Toluene	1.07	8.441	.	.	.
5.	C2-Benzene	1.02	11.596	.	.	.
6.	mp-Xylene	1.02	11.847	.	.	.
7.	o-Xylene	1.02	12.590	0.01	0.01	0.01
8.	Aniline	0.75	15.486	0.30	0.28	0.28
9.	Phenol	0.56	15.784	20.18	25.40	25.38
10.	C3-Benzene	1.00	16.573	0.06	0.05	0.05
11.	Indane	1.00	16.940	.	.	.
12.	Indene	1.00	17.206	.	.	.
13.	o-Cresol	0.69	17.710	7.71	7.88	7.87
14.	mp-Cresol	0.69	18.355	28.52	29.13	29.11
15.	Guaiacol	0.57	18.607	2.13	2.63	2.63
16.	C2-Phenol	0.75	19.056	0.47	0.44	0.44
17.	C2-Phenols	0.75	20.201	0.01	0.01	0.01
18.	C2-Phenol	0.75	20.238	2.58	2.42	2.42
19.	C2-Phenol	0.75	20.697	2.38	2.24	2.24
20.	C2-Phenol	0.75	20.777	4.06	3.82	3.82
21.	Naphthalene	0.90	21.049	0.48	0.38	0.38
22.	C1-Guaiacol	0.60	21.185	0.11	0.13	0.13
23.	Catechol	0.50	21.547	1.89	2.66	2.66
24.	C3-Phenol	0.86	22.343	0.25	0.20	0.20
25.	C3-Phenol	0.86	22.507	0.36	0.29	0.29
26.	Quinoline	0.56	22.595	0.05	0.07	0.07
27.	C1-Catechol	0.63	23.105	2.47	2.76	2.76
28.	C3-Phenol	0.86	23.226	0.24	0.19	0.19
29.	C3-Phenol	0.86	23.340	0.22	0.18	0.18
30.	2-Methylnaphthalene	1.00	23.919	0.28	0.20	0.20
31.	1-Methylnaphthalene	1.00	24.288	0.56	0.39	0.39
32.	C2-Catechol	0.76	25.305	1.45	1.35	1.35
33.	Biphenyl	0.92	25.903	0.09	0.07	0.07
34.	C2-Catechol	0.76	26.028	1.74	1.62	1.62
35.	Acenaphthene	0.90	28.285	0.07	0.05	0.05
36.	Dibenzofuran	0.90	28.969	0.13	0.10	0.10
37.	Naphthol	0.85	29.036	0.73	0.61	0.61
38.	Phenanthrene	0.94	34.300	0.15	0.11	0.11
39.	Fluoranthene	0.93	39.285	0.03	0.02	0.02
40.	Pyrene	0.93	40.159	0.04	0.03	0.03
	Total A%, wt%, wt%			79.74	85.72	85.73
	# of Peaks, wt counts			32	141.86	

KF-Water = Karl Fischer water; Rf = FID relative response factor; Rt = GC retention time (min); A% = GC area percent; wt% = weight percent; AR = as received; wt counts = sum of A%/Rf;